VOL. L AUGUST, 1913 NO. 2

AMERICAN

CHEMICAL JOURNAL

FRACTIONATION OF CALIFORNIA PETROLEUM BY DIFFUSION THROUGH FULLER'S EARTH[1]

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For several years investigations have been in progress in this laboratory upon the effect produced by diffusion of petroleum oils through fuller's earth. These investigations were pursued in order to obtain some idea of the changes produced in the process of diffusion to which the oils have been subjected in their passage from the place of formation to their present location; also, to gain some idea of the substances present in the natural oil by a separation of the constituents by a process not involving the use of heat, and thereby producing changes by cracking and otherwise. The results obtained when a light oil from Pennsylvania and a heavier oil from Illinois were thus fractionated have already been published.[2] In the present investigation, this method of fractionation was extended to a very heavy petroleum from California. As will be later described, the different fractions obtained by such diffusion were studied with regard to their content of paraffin, benzene, and olefin hydrocarbons, and to the amount of sulphur and nitrogen compounds found in them and in the earth through which they passed. For the sake of comparison, the behavior of mixtures of known amounts of benzene and pure paraffin oil, when allowed to diffuse through fuller's earth, were also studied.

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[1] This research was aided by a grant received from the C. M. Warren Committee of the American Academy of Arts and Sciences.

[2] Gilpin and Cram: "The Fractionation of Crude Petroleum by Capillary Diffusion," THIS JOURNAL, **40**, No. 6, December, 1908. Gilpin and Bransky: "The Diffusion of Crude Petroleum through Fuller's Earth," *Ibid.*, **44**, No. 3, September, 1910.

DESCRIPTION OF OILS USED

California Oil I.—Viscous, brownish black in color; of a syrupy consistency, and failed to flow from a small vessel when cooled to —10°; possessed a disagreeable odor, suggestive of organic sulphur compounds; specific gravity at 20°, 0.912; when distilled, the first fraction came over at 90°, colorless and agreeable in odor; the last fraction came at 380°, brown, disagreeable in odor, resembling garlic, but supposed to be due to hydrides of the hydrocarbons, formed during the cracking of the oil; analysis showed appreciable amounts of sulphur compounds present. This oil came from Kern County, California.

California Oil II.—Less viscous than the first oil, and of less disagreeable odor; specific gravity, taken with a delicate Westphal balance at 20°, 0.8890; when distilled, fractions were obtained from 100° to 350°; contained a small proportion of benzene hydrocarbons and 0.760 per cent. of nitrogen compounds; no trace of sulphur compounds was found. The oil came from Well No. 1, Section 30-30-24, Elk Hills, Kern County.

California Oil III.—Fairly viscous, brownish black oil, of somewhat disagreeable, smoky odor; specific gravity, 0.9118 at 20°; when distilled, fractions were obtained from 105° to 340°, attempts to obtain fractions at higher temperatures resulting in the cracking of the oil, giving fractions ranging around 270°; rich in benzene and olefin hydrocarbons, but entirely free from nitrogen and sulphur compounds; its properties resembled closely those of the first California oil. The petroleum came from Well No. 1, Section 30, Elk Hills, Kern County.

Pennsylvania Oil.—A light, thin, dark brown oil from Venango County, Pennsylvania; possessed an agreeable odor; specific gravity at 20°, 0.8470. This was the same oil that had been investigated by Gilpin and Cram, and Gilpin and Bransky. Between the time when this oil was first studied and its investigation in 1912 and 1913, its specific gravity had increased from 0.810 to 0.8470 by evaporation through the barrel staves.

INVESTIGATION OF CALIFORNIA OIL I

The oil first studied was the heavy petroleum from Kern County, California. A description of this oil, named the California Oil I, is found on page 60.

The method of handling this oil was practically the same as that introduced by Gilpin and Cram and improved by Gilpin and Bransky. The apparatus in which the diffusion was carried out was similar to that employed by Gilpin and Bransky. Two minor additions were made to the apparatus. The first of these was a manometer which recorded pressures from 730 mm. to 0 mm. when attached to the exhaust system. The other was a device which it was found necessary to put in series with the exhaust system, owing to the fact that the exhaust was obtained by use of a large Chapman water pump. Fluctuations in the water pressure were accompanied by fluctuations in the amount of exhaust. The device by which the suction could be maintained uniform for any length of time consisted of a sliding tube with perforations at its lower end, that could be adjusted by raising or lowering in a reservoir of mercury according as lower or higher pressures were desired.

It was found at the start that an oil as heavy as this one could not be made to diffuse of itself by capillarity at room temperatures (19° to 23°). To produce the necessary diffusion, reduced pressures were brought to bear, pressures as low as 12 mm. of mercury being maintained for days at a time.

In the preliminary experiments, sixteen tubes were filled with fuller's earth.[1] The tubes were filled by dropping into them an amount of earth that would form a column about a foot in height. Since all ranges of compactness of the earth were desired, the earth in some tubes was not compressed in any way. In others it was rammed slightly by a rod tipped with a rubber stopper. In a third set, it was rammed fairly hard, and in a fourth as hard as possible. The tubes were then allowed to stand undisturbed for a short while, so as to permit the cushions of air held between layers of the earth to escape. A second column of earth a foot in height was then added, the same degree of packing observed, and the process repeated until the tubes were filled. They were then placed with their lower ends in separate reservoirs of oil, and a reduced pressure of 600 mm. was then applied to the upper ends. This failed to produce any diffusion, as could be determined by the level of the oil in the reservoirs, so the pressure was gradually reduced until 20 millimeters of mercury were registered on the manometer. There was, however, no sign of actual fractionation of the oil in any of the tubes, but, instead, at the low pressure that was employed the oil was drawn up through the earth unchanged in any of its properties.

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[1] This earth, known as "XXF Clay," and the fuller's earth used in later work were obtained by courtesy of the Atlantic Refining Co., Philadelphia, Pa.

An explanation of the failure of the oil to fractionate was found in the high viscosity of the petroleum. The oil, instead of diffusing through each minute particle of earth, was sucked around the particles and emerged unaltered at the top of the tube.

The cause of the high viscosity of the oil was doubtless the very large quantity of bitumen and the complex hydrocarbons present, whose boiling points were as high as 380°. Accordingly, efforts were directed toward reducing the viscosity of the oil by coagulating the bitumen. It was shaken with a solid electrolyte and with a solution of the same, but repeated experiments failed to show any perceptible reduction in specific gravity or viscosity, nor was there any noticeable coagulation of the bituminous material held in suspension in the oil.

It was observed, however, that any rise in temperature of the oil was accompanied by a marked decrease in viscosity. Accordingly, the effect of this reduction in viscosity upon the fractionation of the crude petroleum was next studied. In order to secure uniform conditions, it was deemed advisable to have the reservoirs for the oil and also the lower part of the tubes immersed in a large water bath, the temperature of which could be regulated and maintained uniform by a gas thermostat. An appliance that could withstand the action of the heated water and oil was, therefore, devised. Glass bottles, fitted with water-tight stoppers and safety tubes, could not be employed, for these broke when temperatures above 60° were reached. For the fractionation at high temperatures, each tube was constructed of brass, and was made to fit snugly into a closed reservoir of a liter in volume. Contact between the tube and the neck of the reservoir was made perfect by having a lead washer which was held rigidly between the two by a nut that screwed down upon the neck of the reservoir.

To determine the most desirable temperature at which the experiments should be carried out, the viscosity of the oil was measured at different temperatures. The apparatus was the same as used by a previous experimenter.[1] With the viscosimeter it was found that a measured quantity of the oil used by Bransky diffused at the following rates:

4.5 cc. of Pennsylvania Oil (sp. gr. 0.8470):

	Minutes
At 20°	10.25
At 40°	6.00

When a similar quantity of the California Oil I was run through the viscosimeter, it was found that the time required was vastly greater. The following results were obtained at different temperatures:

Table I

4.5 cc. California Oil I (sp. gr. 0.912)

	Minutes
At 20°	84.0
At 40°	41.0
At 60°	17.5
At 75°	11.3
At 90°	8.1

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[1] This Journal, **44**, No. 3.

From the above results, it is apparent that a temperature of at least 75° is necessary for diffusion, since the viscosity of the oil at lower temperatures was so great as to prevent its fractionation by diffusion. The temperature of 90° was ruled out because at that temperature there was a tendency for the lightest ingredients of the oil to distil off. This was determined by keeping a measured quantity of the oil at 90° for a week. A quantity amounting to about two per cent. was found to distil off. For this reason it was deemed advisable to carry on the diffusion of the oil at 75°.

Accordingly, eight tubes packed with varying degrees of hardness were maintained at 75°, and at the end of nine days these yielded the first fractions of the heavy California oil (specific gravity, 0.912). Nearly 90 liters of the oil had to be used to obtain the four fractions in the amounts shown below:

Table II—First Fractionation of California Oil I

Fraction	Sp. gr.	Quantity Liters
1-A	0.8695[1]	1.2
1-B	0.882	1.4
1-C	0.9025	1.8
1-D	0.904	1.75
	Total	6.15

There was thus secured a small proportion of available fractions. This was obtained, however, only after very great difficulties had been overcome and with a loss of nearly 93 per cent. of the original oil. The results demonstrate, nevertheless, the possibility of fractionating a heavy, viscous petroleum. Owing to the difficulties encountered in working with large quantities of the oil at elevated temperatures, it was decided to discontinue work on this heavy petroleum until more adequate means of handling it under the necessary conditions were at the disposal of the experimenter.

The four fractions from the California Oil I, designated as 1-A, 1-B, 1-C and 1-D, were then analyzed for their sulphur content. Similar determinations were made for the oil retained by the earth.

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[1] All specific-gravity measurements were taken at exactly 20° with a delicate Westphal balance.

Determination of Sulphur Compounds in the California Oil I

The odor of the high-boiling fractions of this oil led to the suspicion that sulphur compounds were present. Accordingly, qualitative tests were made to detect the presence of this element. These tests were as follows:

About 10 cc. of the sample to be tested were heated to boiling in a flask provided with a reflux condenser. About half a gram of metallic sodium was introduced, and the liquid heated to the boiling point for about thirty minutes. After cooling to room temperature, water was gradually introduced through the condenser and the flask shaken until the sodium had gone into solution. The solution of the hydroxide containing the sodium sulphide was separated, and the addition of sodium nitroprusside produced a purplish blue or deep purple coloration. A quicker method for the qualitative determination of sulphur was one that is employed in the petroleum industry. A solution of litharge in concentrated potassium hydroxide solution was prepared. The undissolved litharge was allowed to settle, and the clear solution decanted. Several cc. of the oil to be tested were shaken with a small quantity of the potassium plumbite solution, and the oil allowed to rise. The plumbite solution was colored from pale brown to black, according to the amount of sulphur present.

Quantitative determination of sulphur by the usual Carius method failed, the bombs exploding in every one of the fifteen analyses that were attempted. Carius determinations made in hard glass tubes gave no better results. A modified Carius method was then employed. This was essentially as follows: A weighed sample of the oil was introduced into a Carius tube and 5 cc. of fuming nitric acid were poured upon it. The open tube was then heated for two hours in a water bath at 100°. Five more cc. of the acid were then added, and the heating repeated for two more hours. Then five cc. of the acid were again introduced, the tube was drawn out and sealed, and then heated for two hours in a bomb furnace at 280°. The charge of the tube, when cool, was emptied into several hundred cc. of water, and the sulphur determined as barium sulphate by the usual method. This modified Carius method gave results that were somewhat lower than the results obtained by the methods finally employed. This was probably due to the volatilization of the sulphur compounds when the open tube was heated.

The methods found to be most satisfactory, however, were the Sauer combustion method, described in detail in Morse's Exercises in Quantitative Chemistry (pp. 258–60), and a method by which the oil was oxidized in a flask by concentrated nitric acid and potassium chlorate. The two methods gave concordant results. In every instance duplicate analyses were made, and the mean result given in the table below. The fractions analyzed were those described on p. 64.

Table III—Analysis for Sulphur

Fraction	Sp. gr.	Per cent. sulphur
1–A	0.8695	0.11
1–B	0.882	0.144
1–C	0.9025	0.174
1–D	0.904	0.29
Crude oil	0.912	0.541

In order to see if the proportion of sulphur could be further reduced by filtration through fuller's earth, Fractions A and B were refractionated and the results of the second fractionation were analyzed with respect to their sulphur content. The fractions from A are designated as 1–A 1, 1–A 2 and 1–A 3; those from 1–B as 1–B 1, 1–B 2 and 1–B 3.

Table IV—Second Fractionation: Analysis for Sulphur

Fraction	Sp. gr.	Per cent. sulphur
1–A 1	0.857	0.06
1–A 2	0.8604	0.07
1–A 3	0.869	0.104
1–B 1	0.8625	0.072
1–B 2	0.8771	0.09
1–B 3	0.8803	0.141

The results tabulated above show that there is a gradual absorption of sulphur compounds by the fuller's earth. Those fractions that collect at the top of the tubes have the smallest proportion of the sulphur compounds in them, and the amount increases as fractions lower down are taken. The explanation of the comparatively small amount of sulphur in the uppermost fraction is probably as follows: the original petroleum penetrates a grain of the porous fuller's earth, emerges on the other side and has a portion of its sulphur removed and retained by the earth. The possible mechanism of this selective absorption by the earth is discussed later. The oil then enters another grain of earth, the absorptive action of the earth is repeated, and more of the sulphur is removed. The oil that thus penetrates by diffusion up to the top of the tube has passed through the greatest number of grains of earth and thus contains less sulphur than the oil that has not penetrated so far. Moreover, the oil that follows in the track of the first particle of oil which penetrates the earth finds particles of earth that have already taken up the greatest quantity of sulphur that is possible for them to absorb. Hence the second particle of oil passes through earth that is already saturated with respect to its power to absorb sulphur compounds, and it may pass through unchanged, or nearly so. This accounts for the fact that the fractions that are nearest to the original petroleum have chemical and physical properties that closely resemble those of the crude petroleum.

Judging from the results obtained from the second fractionation, it is probable that if enough of the lighter fractions were available for carrying on several more fractionations, the sulphur could be entirely removed.

In order to show to what extent the earth retained the sulphur compounds which were originally in the oil, the earth from which the oil had been displaced by the addition of water was extracted with ether. By this process, oils were obtained which were heavier than those oils expelled by the addition of water. These were analyzed for sulphur, with the following results:

Table V—Analysis of Oil Retained by Earth

Section of earth	Sp. gr.	Per cent. sulphur
Oil extracted from A	0.8955	0.11
Oil extracted from B	0.9038	0.237
Oil extracted from C	0.9105	0.42
Oil extracted from D	0.927	0.675

These results show that it is undoubtedly the earth through which the oils pass that retains the sulphur compounds. They show, moreover, that the earth in the lowest parts of the tube absorbs so much of the sulphur compounds from the oil that passes through them that the proportion of these compounds in the lower end of the tube indicates a concentration that is greater than that in the original petroleum.

INVESTIGATION OF CALIFORNIA OIL II

In working with the heavy California petroleum from which the fractions described above were obtained by diffusion at elevated temperatures, it was pointed out that such fractionation was exceedingly difficult to effect, and at an enormous loss of petroleum. Owing to these results a lighter oil from the same locality was secured. This lighter oil was the one described as the California Oil II (see p. 60). Its properties were somewhat different from the oil first studied. The principal physical differences noted were viscosity and specific gravity, the latter being 0.889 in contrast to 0.912, that of the California Oil I. The viscosity was taken at various temperatures with the following results:

Table VI—Viscosity Measurements of California Oil II (4.5 cc. Run Through)

Temperature of oil	Time Minutes
20°	24.0
30°	17.1
40°	12.2
50°	9.1

It was decided to work with this oil at room temperature, owing to the difficulties arising from the fractionation of large quantities of oil at elevated temperatures. Attention was then turned toward the problem of finding the length of tube most desirable for fractionating an oil of specific gravity 0.889 at 20°.

It was necessary, in addition, to ascertain the proper amount of pressure that should be brought to bear to bring about diffusion. For this purpose glass tubes of 3.2 cm. in diameter and varying in length from 30 to 150 cm. were employed. The object in using glass tubes was to enable the observer to see to what extent fractionation was taking place as the amount of pressure on the tubes was changed. It was soon found that a fractionation of the petroleum could be produced working at room temperatures. While the results obtained were not as satisfactory as those obtained with light Pennsylvania oil of specific gravity 0.8470, they demonstrated the possibility of fractionating an oil of specific gravity 0.889 by diffusion through fuller's earth at ordinary temperatures. The yield of available fractions, however, amounted to only twenty per cent. of the oil used, while in the case of the lighter Pennsylvania oil, it was 45 to 50 per cent. of the petroleum used.

The length of tube that gave the most satisfactory results was found to be about 90 cm. The degree of compactness of the earth that gave best results was obtained by tapping the sides of the tube, and refraining from ramming, as all previous packing had been done. A column of earth a foot long was introduced into the tube, and it was tapped lightly on its side until the top of the column presented a firm surface.

The method employed in extracting the oil from the earth into which it diffused consisted in taking measured sections from the earth[1] after it had been carefully emptied into a cylinder that was split longitudinally, and adding water to each section. The water formed a thick emulsion with the earth and expelled a part of the oil, retaining, however, an oil that was heavier than that expelled. It was noticed that the lighter oils were displaced in much greater proportion than were the heavier oils, for the earth showed a tendency to remain in mechanical combination with the oil, holding almost

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[1] The section of earth from the uppermost part of the tube was called A, and the oil extracted therefrom called 2-A. The next lower section was called B, and its oil 2-B, etc.

100 per cent. if the specific gravity approached 0.9. When an examination of the oil retained by the earth was desired, the oil was extracted from the dried earth by ether. By the ether extraction an oil of different physical and chemical properties was secured. This proved that the fractions obtained by displacement of the oil by water did not represent the actual fractions formed during diffusion through the earth, but only a small part of such fractions.

The method of securing fractions of oil by displacement by water was then dispensed with and another method introduced. This consisted in allowing the oil to diffuse to the top of the tube and then letting it overflow into small tubes of about 70 cc. capacity. The oil that first overflowed and collected in the upper reservoir constituted the first fraction. The first fraction was usually very light in color and specific gravity. As the diminished pressure continued to be applied, a heavier oil began to flow into the upper reservoir. When a change in color was noticeable, the reservoir was emptied or exchanged for another, and the pressure was temporarily cut off from the tube by means of pinchcocks while the change was being made. The second fraction was then collected until a change in color was noticed, and so on with a third, until an oil that was colored brown by the bitumen of the petroleum drained into the upper reservoir. The reduced pressure was then cut off, the tubes cleaned and refilled with fresh fuller's earth, and the process repeated.

By repeated experiment, the amount of pressure that gave the best results was determined and regulated as follows: the tubes were allowed to stand in the reservoirs of petroleum for abour 24 hours, without any reduced pressure being applied. Then, for a period of about three days, the pressure was gradually reduced until the manometer registered 650 mm. of mercury. After being maintained at this height for several days, the pressure was then lowered to 500 mm. and kept there until the first fractions overflowed into the upper reservoirs. When this pressure failed to draw up a slow, steady stream of oil into the reservoirs, it was still further reduced, usually being made as low as 200 mm., by the time that the last available fraction had been collected.

By this method of operating, the California Oil II was found to be capable of fractionation into five distinct fractions. The lightest, termed Fraction 2–A, was of specific gravity 0.8264; the heaviest, 2–E, 0.8737, showing a wide range in density (see p. 72).

The basis upon which the various fractions were differentiated was their color, as it was observed that the depth of color was an approximate measure of the specific gravity of the oil.

The fractions 2–A to 2–E were examined for nitrogen, and all of them showed signs of its presence. Careful analyses of these were then made, and similar analyses of the earth in various parts of the tube were made. Fractions 2–A and 2–B were then subjected to a second fractionation, and the results also studied with regard to their nitrogen content.

Determination of Nitrogen Compounds in California Oil II

Nitrogen compounds were found to exist in the California Petroleum II to the extent of nearly 0.8 per cent. Accordingly, this oil was subjected to fractionation by the improved method that was adopted by the investigator (see p. 70). This was necessary since the oil was too heavy to be worked by the method of Cram and Bransky unless elevated temperatures were resorted to in order to reduce the viscosity. Besides, it was feared that high temperatures would bring about the loss of the nitrogen compounds by volatilization.

The method for determining the nitrogen was that known as the Gunning-Arnold-Dyer modification of the Kjeldahl method. It is described in detail in Sherman's Organic Analysis (pp. 291–4). It was found necessary to digest the light oils as long as 3 or 4 hours and the heavy ones as long as 8 hours before the contents of the digestion flask became colorless. Another necessary precaution had to be observed in applying heat very gradually to the flask at the beginning of the digestion, otherwise the nitrogenous material distilled off, giving results that were far below those obtained when greater precaution was exercised.

Table VII— Nitrogen Determinations

Fraction	Sp. gr.	Per cent. nitrogen
2–A	0.8264	0.08
2–B	0.8421	0.116
2–C	0.852	0.289
2–D	0.8614	0.315
2–E	0.8737	0.332
Crude oil	0.889	0.761

These results show that the proportion of nitrogen compounds is reduced in the lightest fraction to nearly one per cent. of its total amount. This proportion of nitrogen was still further reduced by the second fractionation of the two lightest fractions. The fractions obtained from 2–A are designated by 2–A 1, 2–A 2, etc. Those from 2–B are designated by 2–B 1, 2–B 2, etc.

Table VIII—Second Fractionation of California Oil II

Fraction	Sp. gr.	Per cent. nitrogen
2–A 1	0.8117	Trace
2–A 2	0.8186	Trace
2–A 3	0.8193	0.03
2–A 4	0.8240	0.06
2–B 1	0.8205	Trace
2–B 2	0.8386	0.045
2–B 3	0.8414	0.09
2–B 4	0.8421	0.109

From the above results it is apparent that the fuller's earth is particularly potent in selectively absorbing nitrogen compounds from the oil. In view of the fact that but two filtrations through the earth succeeded in reducing the amount of nitrogen present to such a small proportion as compared to that in the petroleum, it is probable that a third filtration would have reduced it to zero. A third fractionation would have been made, but lack of workable material rendered this impossible.

The analysis of the oil retained by the earth taken from the upper, middle and lower ends of the tubes showed that the part in the lowest sections of the tube had absorbed the greatest amount of the nitrogen compounds from the petroleum. The oil was extracted from sections of earth, taken at different levels from the tubes, by ether. The ether was evaporated off in an electrical drying oven at 50°.

Table IX—Analysis of Oil Retained by Fuller's Earth

Section of tube	Sp. gr.	Per cent. nitrogen
Upper end	0.8413	0.205
Middle section	0.8655	0.43
Lower end	0.9172	0.94

The concentration of the nitrogen compounds in the lower end of the tubes is apparent. It is noticeable that the percentage of nitrogen here is slightly greater than it was in the original petroleum. This was to be expected, inasmuch as the earth in the lower end of the tube came into contact with the greatest amount of oil and could thus selectively absorb more of the nitrogen compounds than earth in the upper end. Moreover, earth in the upper end came into contact with oil that had already had a portion of its nitrogen compounds removed and could not, for that reason, extract as much nitrogenous material from it as it could from oil that was much richer in nitrogen compounds.

The study of the benzene and olefin hydrocarbons in California petroleum was next contemplated. Before taking this up, it was considered advisable to study with some degree of accuracy the behavior of known mixtures of benzene and pure paraffin oil where such mixtures were allowed to diffuse through fuller's earth. This problem had been investigated before by earlier workers in this field, and certain conclusions arrived at, but a further study of the same, working under somewhat different conditions, was now resumed.

FRACTIONATION OF MIXTURES OF BENZENE AND PARAFFIN OIL

In previous work by Gilpin, Cram and Bransky on the fractionation of crude petroleum, it was noted that there was a tendency for the pure paraffin hydrocarbons to collect in the upper section of the tube through which the petroleum was allowed to diffuse. To investigate this more closely, Gilpin and Bransky studied the behavior of mixtures of benzene and paraffin oil, such mixtures being of definitely known composition, and plotted their results in curves that showed the relative amounts of benzene and paraffin oil that collected in all parts of the tube. The curves show, moreover, that the proportion of benzene decreases gradually as one passes from Grade F (the oil from the lowest section of the tubes) to Grade C (the oil from the third section of the tubes), Grade A being considered that fraction from the uppermost part of the tubes. Above Grade C, there is a sharp decrease in the proportion of benzene, the same dropping far below the proportion in the original mixture that was put into the reservoir. It was also noted that the curves representing the specific gravities of the various sections were about parallel with those representing the percentages of benzene. This was to be expected, since the benzene was of considerably higher specific gravity than the paraffin oil. The tubes employed measured five feet six inches in length.

With the view to determine more accurately the exact location of the break in the curve, and to ascertain if it was a function of the length of the tube, investigation along this line was begun by the authors. In order to study the latter problem, it was decided to use shorter tubes, those of two feet nine inches in length being chosen. Correspondingly smaller sections of earth were taken, and the oil was displaced from them by the addition of water.

The benzene used was of specific gravity 0.879. The method of analysis used to determine the proportion of benzene and paraffin oil in each fraction consisted in shaking 10 cc. of the oil with three or four times its volume of concentrated sulphuric acid, until all of the benzene had been sulphonated. Then the shaken material was poured into a burette and allowed to stand until all the paraffin oil mechanically held in combination with the acid had separated out.

To determine the length of time necessary for shaking in order to remove all the benzene, 10 cc. of benzene were mixed with an equal quantity of pure paraffin oil and the mixture shaken with four times its volume of concentrated sulphuric acid in a machine that agitated the mixture about 450 times per minute. The amounts of benzene that were absorbed after definite periods of time were as follows:

Table X —Action of Sulphuric Acid on Benzene and Paraffin Oil

Time of shaking Minutes	Per cent. benzene absorbed
15	52.1
30	79.0
45	91.4
60	100.0

All samples for analysis were, therefore, shaken for more than an hour, until further shaking failed to reduce the volume of the oil.

The paraffin oil used was a light, pale yellow oil of very disagreeable odor. Its specific gravity was 0.7895 at 20°. After purification by the method described below, the specific gravity became 0.7775. The oil was purified as follows: A quantity was agitated with one-third its volume of concentrated sulphuric acid for 6 hours in two 2-liter bottles that revolved slowly about an axis placed between the two. The acid became dark brown, and the evolution of sulphur dioxide indicated chemical action. The acid was then drawn off in a large separatory funnel and a fresh supply added to the oil. This was again agitated for six hours and separated off as before. By this process the volume of oil decreased 9.3 per cent., and lost its disagreeable odor and became colorless. It was then shaken with a small quantity of dilute alkali until neutral, washed with water, and finally shaken for several hours with calcium chloride, and filtered. By repeated tests it was shown that the oil, after this treatment, did not decrease in volume when shaken with sulphuric acid.

Mixtures of benzene and pure paraffin oil were then allowed to diffuse through fuller's earth. The earth in the tubes had been as tightly packed as it was possible to secure by ramming the earth with a rod tipped with a rubber stopper. The proportions of benzene and paraffin oil in the mixtures were as follows:

Name applied to mixture	Per cent. benzene	Per cent. paraffin oil
Series No. 5	20	80
Series No. 6	33	67
Series No. 7	50	50
Series No. 8	75	25
Series No. 9	20	80
Series No. 10	33	67
Series No. 11	50	50
Series No. 12	20	80
Series No. 13	75	25
Series No. 14	20	80

Sections of varying lengths, as shown in the tables accompanying the curves (pp. 77 to 83), were taken, and the oil was displaced by addition of water (in Series No. 5 to No. 8, inclusive), by extraction with ether (Series No. 9), or by letting the oil overflow into upper reservoirs by the new method described on page 70 (Series No. 14).

The sections of earth from which the oil was extracted were made considerably smaller than similar sections taken by Bransky in his work. The uppermost section, called A, varied in length from 25 to 12 cm. The fraction of oil that it yielded was called 5–A, 6–A, according to the series to which it belonged. The next lower section of earth, usually a little shorter than A, was called B. Its oil was termed 5–B, 6–B, or 7–B, according to the series to which it belonged. The short tube and short sections of earth from which the oil was extracted were chosen so as to locate more accurately the point at which a sharp decrease in the amount of benzene occurred. This point of sudden change was found to be invariably located from 20 to 40 cm. from the top. The specific gravity of each fraction of the oil was taken for the first five tubes. Since this in every case was a function of the proportion of benzene and paraffin oil present, it was discontinued after the first five series were run.

Series No. 5 consisted of the following: A tube was filled with earth and the reservoir below filled with 500 cc. of a mixture of 20 per cent. of benzene of specific gravity 0.879 and 80 per cent. of paraffin oil of specific gravity 0.7775. When diffusion had taken place, the fractions were analyzed as before described, and it was found that the break in the curve occurred at about 35 cm. from the top. The specific gravity of that fraction that contained least benzene was the lowest. It was noticeable that the proportion of benzene to paraffin oil was nearly a constant, until the point B was reached (see Fig. I).

Table XI—Series No. 5

Benzene, 20 per cent. Paraffin Oil, 80 per cent.
Rose to a height of 88 cm.

Fraction	Cm.	Cc.	Sp. gr.	Per cent. benzene	Per cent. paraffin
5–A	20	46	0.787	10.4	89.6
5–B	15	44	0.790	19.1	80.9
5–C	15	43	0.791	21.3	78.7
5–D	15	36	0.792	21.0	79.0
5–E	12	30	0.792	21.3	78.7
5–F	11	39	0.795	23.3	76.7

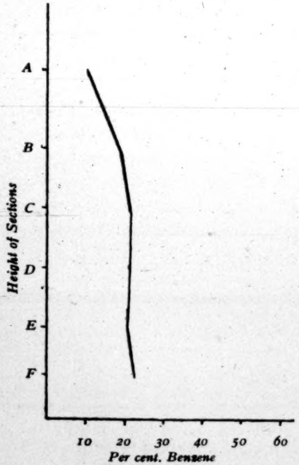

Fig. I.—Series No. 5

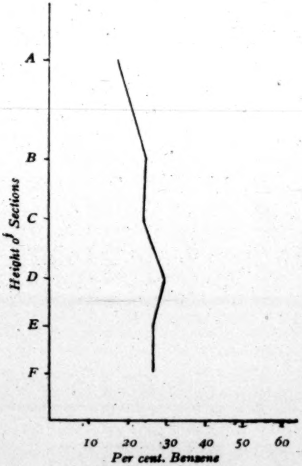

Fig. II.—Series No. 6

In Series No. 6 there was not noticed as marked uniformity in specific gravity or in the proportion of benzene to paraffin oil as in Series No. 5. The break in the curve occurred about 25 cm. from the top (see Fig. II).

Table XII—Series No. 6

Benzene, 33 per cent. Paraffin Oil, 67 per cent.
Rose to a height of 95 cm.

Fractions	Cm.	Cc.	Sp. gr.	Per cent. benzene	Per cent. paraffin
6–A	25	31	0.725	18.4	81.6
6–B	15	38	0.798	25.7	74.3
6–C	15	42	0.798	25.3	74.7
6–D	12	38	0.799	25.9	74.1
6–E	12	35	0.7995	27.3	72.7
6–F	12	45	0.799	27.0	73.0

Series No. 7, with equal quantities of benzene and paraffin oil, gave a curve that broke sharply at Section B, 16 cm. from the top. Up to this point the amounts of the two oils remained nearly constant (see Fig. III).

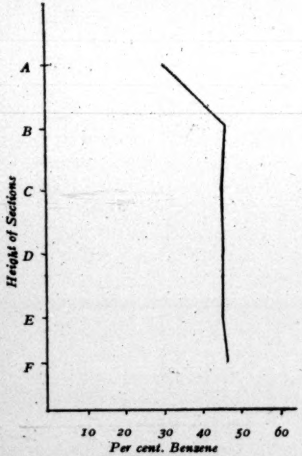

Fig. III.—Series No. 7

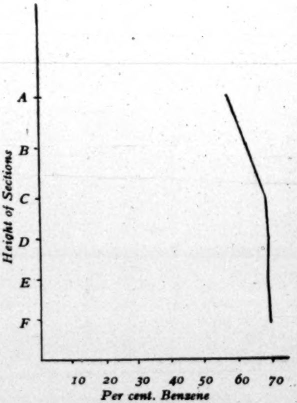

Fig. IV.—Series No. 8

Table XIII—Series No. 7

Benzene, 50 per cent. Paraffin Oil, 50 per cent.
Rose to a height of 90 cm.

Fractions	Cm.	Cc.	Sp. gr.	Per cent. benzene	Per cent. paraffin
7–A	16	21	0.8023	30.5	69.5
7–B	16	34	0.8155	47.0	53.0
7–C	16	44	0.8160	45.8	54.2
7–D	16	50	0.8165	45.7	54.3
7–E	12	48	0.8165	45.7	54.3
7–F	12	53	0.817	47.2	52.8

In Series No. 8 the break was not such a sharp one, and occurred about 30 cm. from the top (see Fig. IV).

Table XIV—Series No. 8

Benzene, 75 per cent. Paraffin Oil, 25 per cent.
Rose to a height of 84 cm.

Fractions	Cm.	Cc.	Sp. gr.	Per cent. benzene	Per cent. paraffin
8–A	15	25	0.832	58.1	31.9
8–B	15	37	0.833	64.5	35.5
8–C	12	38	0.8385	69.0	31.0
8–D	12	44	0.839	69.8	30.2
8–E	12	43	0.839	69.7	30.3
8–F	12	51	0.842	70.1	29.9

In order to determine whether the proportion of benzene to paraffin oil in the fractions was affected by the displacement of the oil by water, the fractions secured from Series No. 9 were extracted with ether. The results plotted in the curve on page 80 show that the water plays no part whatever in the action. The break in the curve, showing a sudden sharp decrease in the proportion of benzene to paraffin oil, occurred in about the same locality.

Table XV—Series No. 9

Benzene, 20 per cent. Paraffin Oil, 80 per cent.
Rose to a height of 70 cm.

Fractions	Cm.	Cc.	Per cent. benzene	Per cent. paraffin
9–A	12	44	8.9	91.1
9–B	12	34	18.4	81.6
9–C	12	38	20.0	80.0
9–D	10	37	21.7	79.3
9–E	10	39	21.3	79.3
9–F	10	44	22.1	78.9

In Series No. 10 and No. 11 (Figs. VI and VII) the individual fractions were analyzed immediately after the displacement of the oil in the earth by water. This was done so as to avoid any possible loss of either oil by evaporation. The same general characteristics are apparent in the curves that express the results of the fractionation.

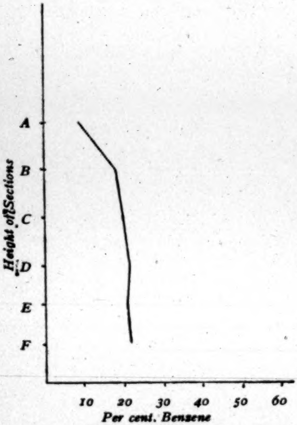

Fig. V.—Series No. 9

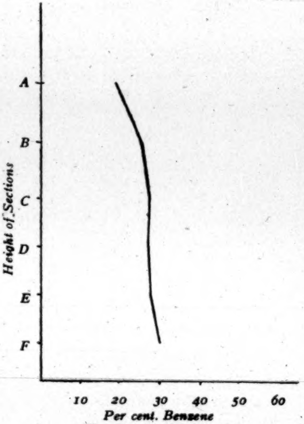

Fig. VI.—Series No. 10

Table XVI—Series No. 10

Benzene, 33 per cent. Paraffin Oil, 67 per cent.

Rose to a height of 81 cm.

Fractions	Cm.	Cc.	Per cent. benzene	Per cent. paraffin
10–A	15	36	20.1	79.9
10–B	15	53	26.2	73.68
10–C	12	45	28.0	72.0
10–D	12	52	27.7	72.3
10–E	12	42	28.1	71.9
10–F	10	37	30.4	69.6

Table XVII—Series No. 11

Benzene, 50 per cent. Paraffin Oil, 50 per cent.
Rose to a height of 74 cm.

Fractions	Cm.	Cc.	Per cent. benzene	Per cent. paraffin
11–A	15	35	32.1	67.9
11–B	12	42	47.1	52.9
11–C	12	37	47.1	52.9
11–D	10	41	46.9	55.1
11–E	10	36	50.4	49.6
11–F	10	35	50.9	49.1

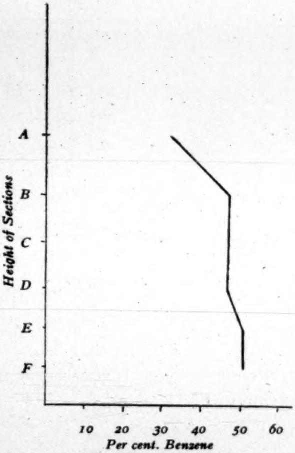

Fig. VII.—Series No. 11

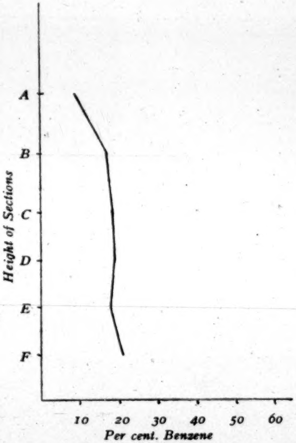

Fig. VIII.—Series No. 12

In all tubes up to Series No. 12 the oil was drawn up to a height under two feet nine inches. Although tubes five feet nine inches long were used, the quantity of oil placed in the reservoir was such as allowed only the lower half of the earth in the tube to become impregnated. In order to avoid the possibility of the more volatile oil evaporating into the dry earth above it, tubes of 2 feet 9 inches in length were used for Series No. 12 and No. 13. The curves representing the results from these series (pp. 81 and 83) show that this precaution failed to produce any noticeable difference in the proportion of benzene and paraffin oil or in the characteristic behavior of the fractions that were obtained by diffusion through fuller's earth.

Table XVIII—Series No. 12

Benzene, 20 per cent. Paraffin Oil, 80 per cent.

Rose to a height of 80 cm.

Fractions	Cm.	Cc.	Per cent. benzene	Per cent. paraffin
12–A	15	31	9.5	90.5
12–B	15	40	16.8	83.3
12–C	12	54	18.6	81.4
12–D	12	52	18.8	81.2
12–E	12	56	18.0	82.0
12–F	12	53	21.1	79.9

Table XIX—Series No. 13

Benzene, 75 per cent. Paraffin Oil, 25 per cent.

Rose to a height of 80.5 cm.

Fractions	Cm.	Cc.	Per cent. benzene	Per cent. paraffin
13–A	15	30	60.0	40.0
13–B	15	41	69.1	31.9
13–C	12	37	72.8	27.2
13–D	12	41	71.3	28.7
13–E	12	47	74.0	26.0
13–F	12	48	74.9	25.1

Series No. 14 was set up to test out the improved method of fractionating by means of the earth. Eight hundred cc. of a mixture of 20 per cent. benzene and 80 per cent. paraffin oil were drawn up through tightly packed fuller's earth, and six fractions of 50 cc. each were collected in the upper reservoir. The first of these was designated 14–A, and the last 14–F. The six fractions were separately analyzed and the results plotted in a curve (see p. 83).

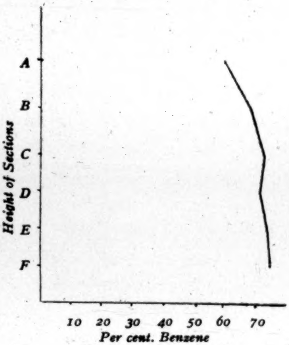

Fig. IX.—Series No. 13

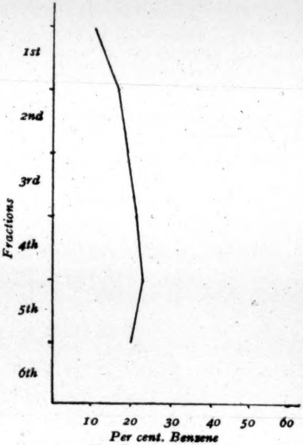

Fig. X.—Series No. 14

Table XX—Series No. 14

Benzene, 20 per cent. Paraffin Oil, 80 per cent.

Fractions	Cc.	Per cent. benzene	Per cent. paraffin
14–A	50	10.9	89.1
14–B	50	17.1	82.9
14–C	50	19.4	80.6
14–D	50	21.6	78.4
14–E	50	23.0	77.0
14–F	50	20.0	80.0

Extract of Earth Left in Tube

Fractions	Cm.	Cc.	Per cent. benzene	Per cent. paraffin
Upper half	70	215	15.9	84.1
Lower half	70	225	13.8	86.2

It was found that the proportion of benzene in the first fraction was the lowest, and that it gradually increased in the subsequent fractions. The curve above shows that the increase in benzene in the successive fractions is more gradual than when the oil was obtained by being expelled by water. There was, however, a marked increase in the amount of the benzene after the first 50 cc. had been drawn off. This corresponds to the increase indicated by the curves in every series that was run, and thus it appears that the new method of working gives the same results as the other methods of manipulation.

These results show that the degree of fractionation is not a question of the absolute height of the earth through which the oil passes, but of the relative height. The advantage, however, of using long tubes is that more material can be obtained and a greater number of fractions between the two extremes are possible.

FRACTIONATION OF CALIFORNIA OIL III

With a view to studying in some detail the fractionation of a heavy California petroleum, a tank of this material was secured from Kern County. It had a specific gravity of 0.9118 at 20°, and resembled in physical properties the California Oil I. A description of this oil, termed California Oil III, is found on page 60. In order to find the best conditions for securing large workable fractions of this oil, preliminary work was carried on by means of glass tubes so as to enable the investigator to observe the progress of the fractionation. The glass tubes measured 1.25 inches in internal diameter, and varied in length from two to five feet. The object of this was to find the length of tube which would give a maximum yield of workable fractions.

The tubes were filled with a fine-grained fuller's earth known as XXF clay. The method of packing these by ramming with a rod tipped with a rubber stopper was abandoned since this gave varying degrees of hardness, while strict uniformity was desired. It also failed to remove the cushions of air that persisted in remaining between layers of the earth, and these, it had been found in earlier work, were a grave source of trouble. Instead, the earth was run into the tubes until they were full. Then the tubes were tapped on their sides throughout their length until the earth failed to subside. More earth was added to fill in the space left vacant by the earth that had settled, and they were tapped again until further subsidence ceased.

With tubes packed as indicated above, the fractionation of the oil by suction was commenced. It was soon apparent that the amount of fractionation by using the fine-grained earth would be exceedingly small, and that it would possibly require four or five weeks' suction to bring the oil to the top of the longer tubes, so the effect of using a coarse-grained earth was suggested. Accordingly, fuller's earth of the size 30 to 60 mesh was secured. The tubes were packed uniformly by the method above described, and placed in the reservoirs. The pressure was reduced to 650 mm. of mercury. Even at this slight reduction in pressure, the oil was drawn up through the tubes, the products showing, however, no signs of fractionation. Accordingly, after repeated experiments, the tubes were allowed to stand 48 hours with no suction applied, and then the pressure on the top of the tubes was reduced to 730 mm. With this, the oil started to rise slowly and steadily through the earth, the uppermost part showing signs of marked fractionation. When the oil had risen to the height of about 18 inches, the pressure was reduced to 700 mm.; at a height of 3 feet, it was reduced to 650 mm.; and above 4.5 feet it was maintained at 600 mm. until all of the available oil was drawn over into the upper reservoirs. By use of the coarse-grained fuller's earth the time required for fractionation of a series of tubes was found to be from ten to twelve days. The fractions of oil that were drawn up and collected were classified on the basis of color. With this as a criterion, six distinctly different fractions were obtained, and these showed a wide range in color and specific gravity.

The total amount of these six fractions was, however, only 15 per cent. of the oil put into the lower reservoir, there being a loss of 85 per cent. due to the speedy darkening of the earth by the bitumen present in the petroleum. Results, with a brief description of the fractions obtained, are tabulated below:

Table XXI—Preliminary Fractionation of California Oil III

Fraction	Sp. gr.	Description
1	0.8364	Nearly colorless; pale green fluorescence
2	0.8449	Pale yellow; pale green fluorescence
3	0.8609	Yellow; quite fluorescent
4	0.8701	Light brown; strong fluorescence
5	0.8770	Brown; strongly fluorescent
6	0.8866	Dark brown; deep green fluorescence

These were the first results that were ever obtained with an oil of as high specific gravity and viscosity as this one, for all investigations carried on at room temperature with an oil of this high density had failed thus far to produce any results. When these six fractions were next examined as to their chemical properties, it was found that the diffusion through the earth had not only lowered the viscosity of the oil, removed the bitumen, and thereby greatly decreased the specific gravity of the oil, but it had also absorbed from the petroleum a large proportion of benzene and olefin hydrocarbons.

The amounts of the two last-named ingredients were ascertained by treatment of the oil with concentrated sulphuric acid. This did not determine the benzene and olefin hydrocarbons separately. It is fair to assume that the concentrated acid acted upon the other materials in the oil, but that it removed all the benzene and olefin hydrocarbons was conclusively proved by a method described later on.

The method by which the benzenes plus the olefins were determined was as follows: Ten cc. of each fraction were carefully measured from a burette. The light oils were shaken with three times their volume of concentrated sulphuric acid until no further diminution in the volume of the oil occurred. The shaking was accomplished in a machine that vibrated 400 times per minute. The bottles containing the oil thus treated were emptied into burettes, rinsed with a few cc. of acid and allowed to drain overnight. The oil not acted upon rose in this time above the acid, and could be read off and directly translated into percentages of paraffin hydrocarbons present.

This last statement is based upon the fact that paraffin hydrocarbons are not acted upon by cold, concentrated sulphuric acid, while the benzene and olefin hydrocarbons react with the acid to form sulphonic and alkylsulphuric acids, respectively. That the benzene and olefin hydrocarbons were entirely removed by two hours' agitation with a large excess of sulphuric acid was proved by the absence of these compounds in the oil after it had been acted upon. The test for benzene was the action of nitric acid to give nitro derivatives and the subsequent reduction to give amino compounds. The tests for olefin were the direct addition of bromine and the action of alkaline permanganate solution.

The treatment of the heavier oils with sulphuric acid was somewhat different from that of the light oils, in that in the case of the former the action of the acid produced a mixture so dark and viscous that the line of demarcation between the acid and the unabsorbed oil was invisible. Therefore, the sample of heavy oil was treated in one of the following ways:

I. It was mixed with twice its volume of pure paraffin oil that had been treated previously with concentrated acid until none of it was absorbed by further action of the acid upon it (see p. 75). The diluted oil was then shaken for five hours or more with three times its volume of acid until further diminution in volume of the oil ceased;[1] or

II. The sample was shaken with thirty cc. of sulphuric acid for two hours, and the mixture was thinned out by diluting with twenty cc. of the paraffin oil, shaken for a few minutes, drained into the burette, and the amount of benzenes and olefins present determined by difference between thirty cc. and the amount of oil unabsorbed by the acid. The methods of determining the sulphuric acid absorption gave results that were concordant to within 0.5 per cent. The accuracy of the analysis by this method was within one per cent., as was proved by analysis of known mixtures.

The percentages of benzene and olefin hydrocarbons that were found in the various fractions of the oil (see p. 86) were found to vary from 5.15 per cent. to 27.7 per cent., as shown in the following table:

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[1] For diluting the 10 cc. sample for analysis and shaking with 90 cc. of sulphuric acid, it was necessary to have a burette of over 120 cc. capacity. This was secured by blowing a bulb of 80 cc. at the lower end of a 50 cc. burette, leaving a volume of about 40 cc. above by which to read the amount of oil that was not acted upon.

Table XXII—Preliminary Determination of Benzenes and Olefins in California Oil III

Fractions	Per cent. benzenes and olefins
1	5.15
2	10.4
3	15.2
4	16.8
5	20.6
6	27.7

It is thus seen that the earth through which the oil passed exerted an absorptive effect upon the benzene and olefin hydrocarbons. This effect has been termed selective absorption or adsorption, by which is meant that the earth exerts an action upon the complex oil by which it retains an appreciable quantity of certain of its ingredients. It is not a filtration effect, for when the petroleum is drawn quickly through coarse or fine fuller's earth by means of low pressure, it filters through, depositing any solid matter that may be suspended, but being otherwise unaltered.

If the action of the earth is explained as a phenomenon of adsorption, the statement might be made that the separation of the bituminous material from the petroleum was by the coagulation and adhesion of the bitumen to the very extensive internal surface that the grains of fuller's earth possess. For it is a well-known fact that porous media like charcoal, dried clays, colloidal and finely divided metals, platinum sponge, etc., possess an enormous amount of surface energy, due to the forces that are active at their extensive surface, and that such substances show the phenomenon of adsorption to a marked degree. The separation of the bitumen, carrying with it the benzene hydrocarbons, the olefins, the sulphur and nitrogen compounds, may thus be regarded as a special case of adsorption.

If the bitumen is considered as existing in the colloidal condition, the effect of the internal surface of the fuller's earth could be explained as bringing about the coagulation of the colloidal bitumen into discrete particles which would carry with them all materials in the oil, save the paraffin hydrocarbons. That all the above-mentioned materials are held behind by the fuller's earth has been conclusively established by direct and indirect proof. In retaining the bitumen with benzenes, olefins, nitrogen and sulphur compounds and permitting the paraffin oils to diffuse through, the fuller's earth acts as a dialyzer, proving more or less impervious to the substances held in solution in the paraffin oils, but not so to the solvent itself.

Fractionation of California Oil III

For the more accurate study of the physical and chemical properties of the fractions obtained from this oil, large quantities of these fractions were necessary. Accordingly, a slight alteration was made in the apparatus employed, so as to be able to handle larger quantities. The tubes originally used measured 1.25 inches by 5.5 feet. It was now decided to test out tubes of greater diameter and length, and the size finally adopted was 2.75 inches in diameter by six feet in length. In order to be able to observe the behavior of the oil, a glass tube of the same size was joined in parallel with the tin tubes. With tubes of this diameter it was found that the best results were obtained by using very little suction, and by extending the suction over a period of about two weeks, as the yield of available fractions was found to increase through this method of working. This was ascertained by measuring the amounts of each of the fractions that were obtained from a single tube placed in a measured amount of petroleum. From this tube 14 distinct fractions were secured, the basis of distinction being the color of each. The amounts of each fraction and a brief description of the same are as follows:

Table XXIII—Preliminary Fractionation of California Oil III

Fraction	Amount Cc.	Description
1	35	Colorless, pale blue fluorescence
2	38	Colorless, pale green fluorescence
3	40	Pale yellow, pale green fluorescence
4	40	Yellow, pale green fluorescence
5	48	Yellow to deep orange-brown, increasing green fluorescence as fractions increased in sp. gr. and viscosity
6	45	
7	47	
8	60	
9	65	
10	63	Light to dark brown in transmitted light; fluorescence less pronounced, but still very noticeable
11	75	
12	85	
13	88	
14	110	

The total amount of available fractions was 839 cc. The amount of petroleum used was 3500 cc. The yield was 23.7 per cent.

It is seen from the above figures that the yield of heavier fractions is increasingly greater than that of the lighter oils. It is also to be noted that this slower method of working increased the total yield of available fractions from 15 per cent. to nearly 24 per cent. Fractions that were colored darker than the fourteenth were discarded as being contaminated with too much bitumen.

The fractionation of considerable quantities of California Oil III was then undertaken, and differentiation was made between the various fractions on the basis of specific gravity, a hydrometer small enough to fit into the upper reservoirs being used[1] to indicate the specific gravity approximately. The boiling points of the various fractions were taken at atmospheric pressure. Every fraction was found to be a mixture of oils, for not any of the boiling points remained constant, but, instead, rose through a range of 11 to 35 degrees. In determining the boiling points, 5 cc. of each fraction were taken. In order to get the boiling point of the greatest part of each, i. e., of that part which represented the average of the constituents, one cc. was distilled off, and the boiling point noted during the distillation of the next three cc. The boiling point of the last cc. was not taken. The distillates ranged from a colorless, thin oil with a smoky smell to a thick, dark brown oil of a very disagreeable odor resembling garlic.

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[1] The upper reservoirs were glass tubes 2.5 cm. × 16.5 cm. closed at one end. Two-hole rubber stoppers fitted in the tops which were flanged slightly to give airtight connections.

The fractions from the California Oil III were termed 3–A, 3–B, etc. Those of a second fractionation were termed 3–A 1, 3–A 2, etc. The range of the fractions obtained was as follows:

Table XXIV—Fractionation of California Oil III

Fraction		Sp. gr.	Boiling point
1	3–A	0.8325	160°–195°
2	3–B	0.8347	172°–201°
3	3–C	0.8372	186°–219°
4	3–D	0.8462	210°–231°
5	3–E	0.8524	235°–260°
6	3–F	0.8551	247°–269°
7	3–G	0.8680	256°–280°
8	3–H	0.8781	268°–289°
9	3–I	0.8840	275°–310°
10	3–J	0.8885	284°–317°
11	3–K	0.8903	299°–326°
12	3–L	0.895	311°–328°
13	3–M	0.8972	317°–334°
14	3–N	0.8984	329°–340°
Crude petroleum		0.9118	105°–340°

These results show the very wide range in specific gravity between the first and last fractions of the petroleum under investigation. For comparison, the range of fractions obtained from a lighter Pennsylvania petroleum by Gilpin and Bransky are given in the following table:

Fractionation of Pennsylvania Petroleum

Fraction	Sp. gr.	Fraction	Sp. gr.
A–1	0.8250	D–2	0.8495
A–2	0.8287	D–3	0.8515
B–1	0.8367	D–4	0.8555
B–2	0.8392	E–1	0.8527
C–1	0.8413	E–2	0.8540
C–2	0.8460	E–3	0.8570
C–3	0.8488		
D–1	0.8470		

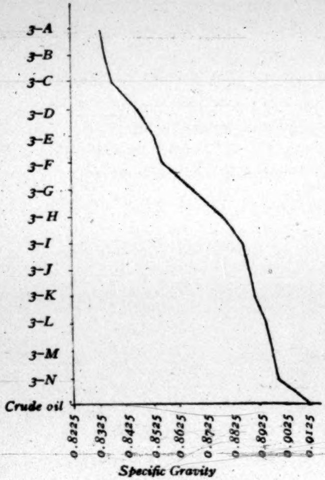

Fig. XI.—California Oil III

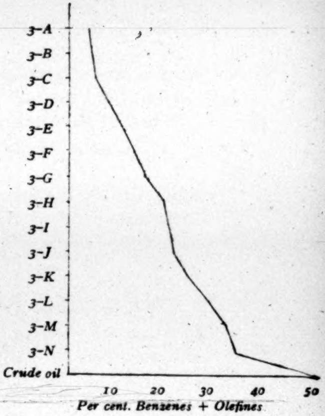

Fig. XII.—Sulphuric Acid Absorption of California Oil III

The range obtained by Bransky's method of working shows specific gravities varying from 0.8250 to 0.8570, as contrasted with the range of 0.8325 to 0.8984 obtained by the present investigator upon the heavy California oil.

Sulphuric Acid Absorption of the California Oil III

The sulphuric acid absorption was determined for the fourteen fractions. The method used was that described on pages 86 to 87. The results are tabulated with respect to the percentage of paraffin hydrocarbons in contrast to that of the benzene and olefin hydrocarbons taken together.

These figures show the great extent to which the diffusion through fuller's earth removes the benzene and olefin hydrocarbons. The first fraction consisted of nearly pure paraffin oils, reaching a degree of purity of 96 per cent., while, by contrast, the crude petroleum contained about 50 per cent. of paraffins.

Table XXV—Sulphuric Acid Absorption

Fraction	Per cent. benzenes and olefins	Per cent. paraffins
3–A	3.7	96.3
3–B	4.14	95.86
3–C	5.1	94.9
3–D	7.44	92.56
3–E	10.13	89.87
3–F	13.06	86.94
3–G	15.2	84.8
3–H	15.8	84.2
3–I	19.89	80.11
3–J	20.6	79.4
3–K	23.47	76.53
3–L	27.9	72.1
3–M	31.45	68.55
3–N	32.72	67.28
Crude petroleum	49.7	50.3

Bromine Absorption of California Oil III

In order to determine the amount of unsaturated or olefin hydrocarbons in the fourteen fractions of this oil, the quantity of bromine absorbed at room temperature (19°–23°) in the dark by a weighed amount of the oil was determined.

The method employed for the determination of the olefin content of the fractions was as follows: A weighed sample of the oil to be analyzed, about 0.6 gram for each determination, was dissolved in fifteen cc. of redistilled carbon tetrachloride. The vessel into which the solution was introduced was a 250 cc. Erlenmeyer flask with a ground glass stopper that fitted accurately and was sunk some distance into the neck of the flask so as to leave a gutter between the neck and the stopper. When the absorption of bromine was taking place, the gutter was filled with a couple of cc. of potassium iodide. It effectually prevented the escape of bromine vapor. The bromine was introduced in the form of a solution in pure carbon tetrachloride. The solution was made practically decinormal by dissolving 3.3 cc. of redistilled bromine in a liter of solvent. Its exact strength was determined by titrating against a known volume of a standard sodium thiosulphate solution. The bromine solution kept best in the dark, but frequent tests of its strength were necessary.

In determining the bromine absorption, a known quantity of the bromine solution was added to the solution of the oil in carbon tetrachloride. The amount added was more than twice that necessary to combine with the total amount of olefins present (as determined by a previous analysis). The flask was closed and shaken, the gutter filled with 2 cc. of a ten per cent. solution of potassium iodide, and the flask allowed to stand in the dark with occasional agitating for thirty minutes. Longer contact of the oil with the bromine gave substitution products as well as addition products, the former being indicated by the presence of hydrobromic acid. After thirty minutes, the flask was brought out of the dark, ten cc. of the potassium iodide solution were added, the flask closed and violently shaken, and the amount of iodine liberated by the excess of bromine present determined by titrating against the thiosulphate solution. Toward the end of the titration, a few cc. of a very dilute starch solution were added to indicate sharply the end point. Repeated shaking of the contents of the flask was necessary during the last part of the titration in order to free the iodine from its solution in the carbon tetrachloride. A blank determination was made parallel with each analysis in order to ascertain how much of the thiosulphate solution was exactly equivalent to the amount of bromine solution that was added. The results were translated directly into the percentage of olefins present in the various fractions and in the crude petroleum.

By the action of concentrated sulphuric acid on the oils, the percentage of benzenes and olefins together was ascertained. The action of bromine gave the percentage of olefins. In order to determine whether the difference between these results gave a value that represented the percentages of benzene alone, an investigation was carried out on the 1st, 5th, 9th and 14th fractions of the California Oil III. After being shaken for several hours with sulphuric acid, they were tested for the presence of benzenes and olefins, and blank results were obtained. Then fresh samples of these fractions were treated with an excess of bromine so as to brominate the olefins present, washed with water, dried and shaken with concentrated sulphuric acid for several hours. By this, an amount of the oil was absorbed which corresponded to the benzenes present. This amount, added to that secured by the action of bromine, gave the true percentages of benzenes and olefins together. The results, however, were in each case a little high, showing that the sulphuric acid must have acted upon the brominated oils, but the difference was not greater than 1.3 per cent. Since the sulphuric acid absorption method was accurate to within one per cent., it was concluded that the difference between the percentages of the oil absorbed by sulphuric acid and that acted upon by bromine could be taken to represent the amount of benzene hydrocarbons present.

The results that justified this conclusion are here given:

Table XXVI

Fraction	Per cent. benzenes	Per cent. olefins	Sum of columns 2 and 3	Per cent. benzenes and olefins by sulphuric acid absorption
3–A	1.09	2.79	3.88	3.7
3–E	5.35	5.05	10.4	10.13
3–I	8.72	12.46	21.18	19.89
3–N	14.03	19.35	33.38	32.72

In the table below, the percentages of the various hydrocarbons present in the oils investigated are given. In the first column are given the designations of the various fractions; in the second are given the mean values of the percentages of the olefins found by determining the bromine absorption (duplicate determinations made in every analysis); in the third are given the percentages of benzenes and olefins taken together, and determined by the sulphuric acid absorption method; in the fourth are given the percentages of benzenes determined by difference between the second and third columns.

These results demonstrate the selective absorption of the fuller's earth in its action upon the olefin hydrocarbons. As is indicated above, the proportion of olefins in the crude oil is

Table XXVII—Proportion of Various Hydrocarbons in Fractions of California Oil III

Fraction	Per cent. olefins	Per cent. benzenes and olefins	Per cent. benzenes
3-A	2.79	3.7	0.81
3-B	3.25	4.14	0.76
3-C	3.62	5.1	1.48
3-D	4.06	7.44	3.38
3-E	5.05	10.13	5.08
3-F	5.84	13.06	7.22
3-G	7.44	15.2	7.76
3-H	8.43	18.8	7.37
3-I	12.46	19.89	7.43
3-J	13.44	20.6	7.16
3-K	14.66	23.47	8.81
3-L	14.81	27.9	13.19
3-M	18.34	31.45	13.11
3-N	19.35	32.72	13.37
Crude petroleum	28.24	49.7	21.47

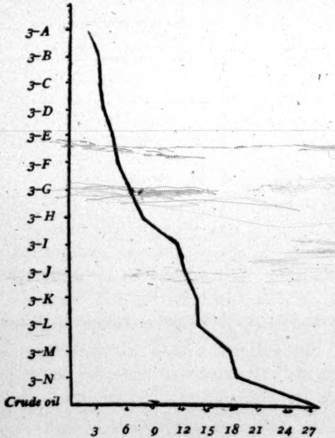

Fig. XIII.—California Oil III

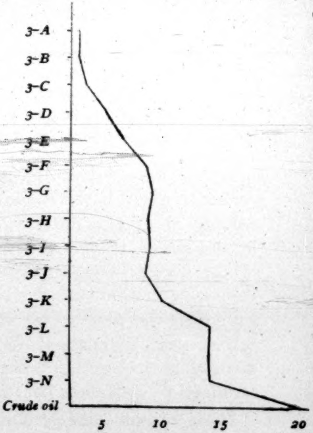

Fig. XIV.—California Oil III

28.24 per cent. In a single fractionation this is reduced to 2.79 per cent. in the first fraction obtained. The gradual increase in the proportion of olefins as the specific gravity of the fractions increases is parallel to the gradual increase, in successive fractions, of all the compounds in the petroleum thus far studied, i. e., of the sulphur compounds, nitrogen compounds, benzene hydrocarbons and olefin hydrocarbons. The results, when plotted in the form of curves, show that there is a noticeable parallelism in selective action of the fuller's earth upon the compounds above mentioned. The curves are found on pages 92 and 96.

In order to determine to what extent the olefins could be removed by further filtration through fuller's earth, a liter of Fraction 3–I was refractionated by means of a tube of smaller diameter. The nine fractions that were obtained were analyzed for their olefin content. The results were as follows:

Table XXVIII—Second Fractionation of California Oil III
(Refractionation of 3–I)

Fraction	Sp. gr.	Per cent. olefins
3–I 1	0.8661	8.55
3–I 2	0.8685	8.93
3–I 3	0.8740	10.06
3–I 4	0.8751	10.82
3–I 5	0.8759	10.77
3–I 6	0.8773	11.40
3–I 7	0.8782	11.67
3–I 8	0.8801	11.79
3–I 9	0.8807	11.89
3–I 10	0.884	12.06

These results demonstrate that a further removal of bituminous material is possible by refractionating a heavy fraction, for there was a slight loss of color occasioned by the diffusion through the earth. Only a part of the olefins was removed, however, by this second fractionation, and the reduction in viscosity was also very slight.

Efforts were made to determine the effect of shaking fractions of oil with large amounts of fuller's earth. Accordingly several portions of Fraction 3–E were shaken with varied quantities of fuller's earth for different periods of time. First, a quantity was shaken with three times its weight of earth for 30 hours and separated from the earth by suction. It was analyzed, with the following results:

Table XXIX—Fraction 3-E Shaken with Three Times Its Weight of Earth

Time in hours	Sp. gr.	Per cent. olefins	Color
20	0.8305	4.01	Yellow
0	0.8524	5.05	Pale orange

When shaken with one-half its weight of earth for periods ranging from 10 to 50 hours, the following results were obtained:

Table XXX—Fraction 3-E Shaken with One-half Its Weight of Earth

Time in hours	Sp. gr.	Per cent. olefins	Color
0	0.8524	5.05	Pale orange
10	0.8524	5.08	Pale orange
20	0.8521	5.00	Pale orange
30	0.852	5.00	Pale orange
50	0.8513	4.90	Same color, but slightly less fluorescence

These results show that the time that an oil is in contact with fuller's earth is of little or no importance as a factor in determining to what extent the earth absorbs certain ingredients from it. The important factor is the amount of earth with which it comes in contact. These experiments substantiate, then, the deductions that are given on page 88 *et seq.*, i. e., that it is the amount of surface of the earth to which the oil is exposed that determines the extent of its absorptive action.

This is in line with the action of those substances whose surface energy is capable of affecting a colloid. That the bitumen in the petroleum investigated exists in this form was proved by the following:

1. There was effected an actual separation of the petroleum into two distinct layers when an electromotive force of 110

volts was impressed upon parts of the oil separated by an unglazed porcelain septum. In order to make the oil conduct the current, one portion was shaken for several hours with one-fourth its volume of a 20 per cent. solution of hydrochloric acid, and another with an equal amount of a 20 per cent. solution of potassium hydroxide. The emulsions formed in this way proved poor conductors, but were sufficiently good to enable the bitumen partially to precipitate out as a brown layer of a very viscous liquid, containing no mineral residue. Its form indicated that the bitumen was held in the original petroleum as a colloid—that type that has been named by Oswald an emulsoid.

2. The high temperature coefficient of viscosity of California petroleum, as shown by earlier experiments (p. 63, Table I), is one of the most marked characteristics of emulsoids, i. e., that type of colloid solution in which the colloid is a liquid in a state of minute subdivision in a liquid medium.

3. The oil and bituminous material that were held back by the fuller's earth could not be removed by mechanical means. For, after the earth had been extracted with ether and carbon tetrachloride until no more could be extracted, it yielded a small quantity of oil upon distillation. This showed that the bituminous material that was in the oil had undergone a change of condition when it was adsorbed by the earth.

SUMMARY

1. The diffusion of petroleum through fine-grained fuller's earth failed to effect the fractionation of the petroleum when the latter was of specific gravity as high as 0.912 at 20°. Raising the temperature of such an oil to 75° made fractionation possible.

2. The effect of such a diffusion of a petroleum containing compounds of sulphur is to separate out the light fractions of the oil containing smaller proportions of sulphur than are found in the original petroleum.

3. The effect of fractionating by means of diffusion through fuller's earth of a petroleum containing nitrogen compounds is to remove the nitrogen compounds from the oil that diffuses

upward through the earth, and to cause them to concentrate in the earth through which the oil has passed.

4. Mixtures of benzene and paraffin oil, when fractionated by capillary diffusion through fuller's earth, give fractions that have marked general characteristics, both chemical and physical, based on the proportions of benzene and paraffin oil in each.

5. The fractionation of a petroleum rich in benzene and olefin hydrocarbons by the diffusion through fuller's earth gives fractions in which the proportions of benzene and olefin hydrocarbons increase regularly with the increase in specific gravity of the successive fractions.

6. An explanation of the above phenomena was found in the conception of the petroleum as an emulsoid, and in the action of the fuller's earth as a dialyzing septum, permitting the free passage of the paraffin oils, and causing by its extensive surface the adsorption and coagulation of the bituminous material, carrying with it the sulphur and nitrogen compounds and the benzene and olefin hydrocarbons.

Johns Hopkins University
May, 1913

REPORT

THE RELATION BETWEEN ELECTRIFICATION AND CHEMICAL REACTIONS AND THE PROPERTIES OF CONDENSATION NUCLEI

1. Phenomena of Condensation of Supersaturated Vapors on Ions. 2. Ionization and Chemical Action. 3. Ions of Small Mobility. 4. The Charging of Neutral Centers and Their Properties. 5. Molecular Aggregates Produced in Gases by Sudden Cooling. 6. The Production of Nuclei. 7. Positive Rays. 8. The Dissociation of Molecules by Moving Ions and the Dynamics of Chemical Reactions in Gases.

Ever since the discovery of the phenomena of electrolysis and the wonderful work of Faraday, scientists have assumed that electrical forces probably play a very important role in the processes involved in chemical reactions. The recent development of our knowledge of the ionization of gases and the phenomena of radioactivity has very greatly strengthened the view that electrons and ions may be products taking part in chemical reactions and the view has been so extended by Thomson and others as to attribute chemical valency to the presence or absence of one or more electrons from an atom or radical.

In order to apply a theory of this kind it is necessary to unravel completely the whole mechanism that is required in order that a given chemical reaction may take place. The experimental evidence shows very clearly that chemical reactions are not nearly as simple as represented in our text-books and that we probably know the exact mechanism in only a few cases.

The relation between electrification and chemical reactions can be considered in three different fields.

(*a*) The study of the processes taking place in solutions led to the atomic theory of electricity and proved a very intimate quantitative relation to exist between the atoms and radicals and the charges which they carry. Investigations in this field of research do not permit us to deal with individual atoms and molecules. In this branch of research we have never isolated quantities of matter containing less than hundreds and perhaps millions of atoms. Indirect evidence in many cases points to the view that molecules in solutions are frequently aggregated together, so that chemical reactions under these conditions must necessarily be much more complex than in gases, where molecules usually exist as independently moving particles. As the study of chemical reactions in solutions has not given us any detailed information concerning the dynamics of chemical reactions, we will pass to a consideration of the phenomena taking place in gases at atmospheric pressure.

(*b*) The early work on ionization indicated that the liberation of electrolytic gases from solutions, the combustion of substances in flames, the oxidation of solids and liquids, and many other phenomena were associated with more or less intense electrification. Naturally, it was expected that a thorough study of these phenomena would lead us to a knowledge of the role played by electrons and ions in various chemical reactions. In order to discuss these phenomena we will have to take up briefly the condensation of vapor on various kinds of nuclei and ions and the properties of "vapor dust" and the various types of ions. The result of this inquiry will show that the processes that take place in flames are very much more intricate than we had at first expected and that as yet we know only a few reactions where it seems that electrons and ions take a direct part.

(*c*) The third field is by far the simplest, and it is in this region that some of the most fundamental of recent discoveries have been made. This field is being most ingeniously explored by J. J. Thomson and most remarkable electrical properties are being discovered concerning the different kinds of ions that constitute positive rays. Stark and others are discovering the nature of the carriers of different types of spectra, so that in the future we shall probably be able to identify the nature of particles in flames, sparks and arcs by the kind of light which they emit. Strutt, Langmuir, Kirkby, and others, are determining the very mechanical processes involved in certain types of chemical reactions taking place at low gas pressures. It seems probable that the new chemistry will deal with atoms, molecules, ions and electrons individually, and that the chemical constants will be calculated as possessing certain statistical values based on the kinetic theory of matter, heat and electricity. In taking up the relation between ionization and chemical reactions we will consider briefly the properties of ions, condensation nuclei and molecular aggregates.

Phenomena of Condensation of Supersaturated Vapors on Ions

Aitken,[1] Coulier,[2] Kiessling,[3] and others, showed that the clouds produced by the lowering of temperature resulting from small adiabatic expansions of damp, dusty air failed to appear if the dust was removed by filtration. The drops in the cloud collected about the dust particles and did not pass through dimensions comparable to that of molecules, where the effect of surface tension would presumably lead to intense evaporation. Phenomena of condensation led R. von Helmholtz, Richarz, and others, to believe that ions could also act as nuclei. The method, used by C. T. R. Wilson,[4] of suddenly cooling a moist gas by adiabatic expansion, so that the gas becomes supersaturated, shows that negative and positive ions act as condensation centers.

When the filtered gas saturated with water vapor is ionized, no cloud is formed until the expansion is 1.25; at this expansion condensation begins to take place on the negative ions. (It would be interesting to work with the proper vapor and the proper pressure to find what expansions would be necessary for ions of different sizes.) The intensity of the rays producing the ionization has no effect on changing the value 1.25. Clouds can be produced several seconds after the ionizing rays have been cut off. The proof that the condensation takes place about the negative ions lies in the fact that the droplets in the fog are all negatively charged and that the production of these fogs is prevented by the removal of the ions.

[1] Nature, **23**, 195, 394 (1880).

[2] J. pharm. chim., **22**, 165 (1875).

[3] Naturw. Verein. Hamburg-Altona, **8**, 1 (1884).

[4] Phil. Trans., **189**, 265 (1897).

After the production and evaporation of a dense fog by an expansion between 1.25 and 1.38, it is found that for a short time drops can be produced by an expansion less than 1.25. The evaporation of the dense fogs has apparently left nuclei (possibly little drops of water) that act like dust particles. Positive ions begin to act as nuclei when the expansion is 1.31 or greater. For eightfold supersaturations dense clouds are formed without the action of an ionizing agent. These droplets are uncharged. J. J. Thomson gives their probable radius as 0.5×10^{-7} cm., this being slightly larger than the size of the drop that forms about an ion (0.3×10^{-7} cm. radius). The amount of supersaturation necessary for these kinds of fogs is the same in air, oxygen, hydrogen and carbon dioxide. Intense ultraviolet light produces clouds in air and oxygen without the necessity of any expansion at all. These clouds are very fine and may last for hours after the light has been removed. This may be due to the formation of hydrogen peroxide or some other substance which lowers the vapor pressure of the drops.

(Much interesting work remains to be done upon the condensation of various vapors at various pressures and temperatures upon ions. Electrons could be experimented upon at low temperatures, the vapor and expansion being suitably chosen. Ions of different kinds, such as recoil atoms, can be used as condensation centers.)

C. T. R. Wilson[1] has succeeded in making visible the tracks of ionizing particles through a moist gas, by condensing water upon the ions immediately after their liberation. The cloud chamber is 16.5 cm. in diameter and 3.4 cm. high, the sides being of glass coated on the inside with gelatin. A Leyden jar discharge through mercury vapor is used to illuminate the clouds formed during the expansion. The spark is produced at a definite interval after the formation of the cloud.

The tracks of the α-particles, as photographed by the above method, are narrow and sharply defined when the α-particles have been shot out just before the expansion. Trails have been photographed for the emanation products in a gas as well as from solids. The tracks are straight over the greater part of the length of the path, but near the ends of the path they are nearly all bent, often abruptly. The bent portion may be 2 or 3 mm. in length. Sometimes the collision of an α-particle seems to give sufficient energy to the particle struck to cause it to ionize by collision, i. e., makes a recoil ray. The formation of these recoil rays should give us considerable knowledge of the nature of the collisions and of the colliding particles. Some α-rays show a gradual bending throughout a large portion of the path.

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[1] P. Roy. Soc., A, **85**, 285 (1911); **87**, 277 (1912).

The β-particles leave tracks that are straight at first and later become curved with many sudden changes in direction. Over considerable distances the ions appear in pairs, but now and then 20 or 30 ions appear together in a closely packed group. The groups are similar to those produced by secondary cathode rays generated by X-rays. The negative ions give rise to a densely packed cluster while the positive ions are more scattered out by the action of the electric field of the expansion chamber. Omitting the clusters, the number of ions is about 32 per cm. length of path at atmospheric pressure. Including the clusters, the number of ions is about double the above number. The clusters may be due to slow cathode rays produced by the β-particles. While α-particles show both a gradual and a sudden bending of their paths, the β-particles show a bending which is generally gradual or cumulative.

The photographs of X-ray ionization do not indicate any effect produced by the X-rays except that of causing secondary cathode rays. Wilson has used a heterogeneous X-radiation and hence has found the secondary cathode rays possessing different lengths of path varying from 0.5 to 1 cm. It would be interesting to find whether a homogeneous X-radiation gave cathode rays of the same velocity.

The secondary cathode rays showed sudden and cumulative changes in regard to the direction of their paths, the latter being the more important. Abrupt deflections occur frequently through angles of 90° or more. The bending is greater near the end of the trail and the end itself is enlarged into a kind of head, possibly due to the path of the corpuscle becoming very irregular. About 5 mm. from the end, the number of ions produced per cm. of track at atmospheric pressure is about 400. At the last 0.5 mm. of one path 4320 ions were counted in one case. The rays appear to start in all directions. The photographs indicate the number of positive and negative ions to be the same.

In considering the chemical effects of the various ionizing radiations it is necessary to know the process of ionization and the nature of the collisions. Methods such as Wilson's should provide a method of finding how ozone, oxides of nitrogen, hydrogen peroxide, etc., are produced by α-, β- and γ-rays.

Condensation in Gases Saturated with Water Vapor

(V_1 is the volume of the gas before expansion and V_2 the volume after expansion. S is the supersaturation of the water vapor after the expansion.) Gas under normal conditions:

	Rainy condensation		Misty condensation	
Gas	V_2/V_1	S	V_2/V_1	S
Air	1.252	4.2	1.38	7.9
O_2	1.257	4.3	1.38	7.9
N_2	1.262	4.4	1.38	7.9
CO_2	1.365	4.2	1.535	7.3
Cl_2	1.3	3.4	1.45	5.9
H_2	1.3	3.4	1.38	7.9

Condensation in Air Ionized by X- and γ-Rays

Observer	Vapor	Ion	V_2/V_1	S
Wilson	Water	—	1.25	4.15
"	Water	+	1.31	5.8
Laby	Ethyl acetate	+	1.48	8.9
"	Methyl butyrate	+	1.33	5.3
"	Methyl isobutyrate	?	1.35	5.2
"	Propyl acetate	+	1.31	5.0
"	Ethyl propionate	?	1.41	7.8
"	Formic acid	?	1.78	25.1
"	Acetic acid	+	1.44	9.3
"	Propionic acid	?	1.34	9.4
"	Butyric acid	?	1.38	15.0
"	Isovaleric acid	?	1.22	6.0
Przibram	Methyl alcohol	+	1.25	3.1
"	Ethyl alcohol	+	1.17	2.3
"	Propyl alcohol	?	1.18	3.0
"	Isobutyl alcohol	?	1.20	3.6
"	Isoamyl alcohol	+	1.22	5.5
"	Chloroform	+	1.54	3.0

Besson[1] has studied the clouds produced in carbon dioxide saturated with water vapor. The following are some of the results obtained by him:

Expansions below 1.30	A few drops
Expansion between 1.30 and 1.32	A few additional drops
Expansion 1.332	Light rain, not very dense
Expansion between 1.332 and 1.40	Gradual increase of the rain
Expansion between 1.41 and 1.44	Rapid increase of the rain

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[1] Compt. rend., **154**, 342 (1912).

Expansion between 1.453 and 1.50	Thick clouds that remain in suspension for a long time. Slow increase in the intensity of the cloud with an increase of expansion
Expansion 1.51	Very thick fog
Expansions above 1.51	The appearance of the fog is not changed

The action of X-rays causes the appearance of rain for an expansion of 1.30, as in the case of air. The addition of a small amount of air results in the appearance of rain for an expansion of only 1.30.

Ionization from Flames

The gases that come from flames of coal gas (whether luminous or not), oxyhydrogen, alcohol, carbon monoxide, etc. (but not of ether), even when the flames are at some distance and the gases have been cooled, show a very considerable conductivity for some time. This conductivity is due to the presence of ions. The ions stick to any dust or small particles that may be in the gas, and then move so slowly that their rate of recombination is very small. McClelland[1] has shown that the mobility of the ions decreases very rapidly as the distance from the flame increases. For the production of this ionization high temperature as well as chemical combination is necessary, and it is possible that chemical reactions themselves are not the cause of the ionization. For instance, hydrogen and chlorine do not conduct even when combining under the influence of ultraviolet light.[2]

From the work of Pouillet,[3] Neyreneuf,[4] Holtz[5] and others among the early workers, it was shown that in a coal-gas flame, where the gas comes in contact with the air, and where combustion is most rapid, the electrification is positive, and is attracted by a negatively charged electrode. The interior of the flames, consisting largely of unburned coal gas, has an excess of negative electricity. Important work upon the electricity developed in flames has been done by Giese[6] and others, an account of which is given by Wiedemann.[7] Franck and

[1] Phil. Mag., **46**, 29 (1898).

[2] Thomson: P. Camb. Phil. Soc., **11**, 90 (1901).

[3] Ann. chim. phys., **35**, 410 (1827).

[4] *Ibid.*, [5] **2**, 473 (1874).

[5] Carl Repert, **17**, 269 (1881).

[6] Ann. chim. phys., **17**, 1, 236, 519 (1882).

[7] Elektricität, **14**, 8, Chap. 4.

Pringsheim[1] have burned hydrogen in chlorine. The mobility of the positive ions thus formed is many times greater than that of the negative ions. Electrons do not appear to exist. The anode fall is greater than the cathode fall, and the unipolar conductivity of the flame is the reverse of that of ordinary flames. Sodium chloride does not give any coloration to such a flame.

The introduction of salt vapors into flames greatly increases their conductivity, especially when the salt is introduced at the cathode. Arrhenius[2] and Wilson[3] have studied the influence of various salts on the conductivity of flames by introducing solutions of the salt into the coal gas by means of a Gouy sprayer. The conductivity of the salt was obtained by getting the difference of the conductivity before and after the salt was introduced. When the concentration of the salt was small, equivalent solutions of all salts of the same metal gave approximately the same conductivity to the flame. The conductivity given by different salts in flames at the same temperature and at the same concentration is as follows:

	Chlorides			Nitrates		
Potential diff.	5.60	0.795	0.237	5.60	0.795	0.237
	Current			Current		
Caesium	123.0	60.5	22.2	303.0	115.0	36.6
Rubidium	41.4	26.4	11.3	213.0	82.4	25.9
Potassium	21.0	13.4	5.75	68.4	29.3	9.35
Sodium	3.49	2.45	1.15	3.88	2.67	1.32
Lithium	1.29	0.87	0.41	1.47	0.99	0.53
Hydrogen	0.75	...	0.27			

G. C. Schmidt[4] considers that the vapors of the halogen salts of zinc, cadmium, aluminium and ammonium conduct electricity while those of mercury, tin, arsenic and organic substances are nonconductors. The conductivity of cadmium salts decreases with the time until a constant value is reached. The other salts usually show an initial increase and then behave like the cadmium salts. The conductivity increases rapidly with rise in temperature and with decreasing pressure.

The mobility of the negative ion in flames at 2000° C. is about 1000 and is independent of the salt in the flame. The mobility of the positive ions of caesium, rubidium, potassium, sodium and lithium is about 62. In heated air, at about 1000° C., Wilson found:

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[1] Verh. d. physik. Ges., **13**, 1911.

[2] Ann. Physik, **42**, 18 (1891).

[3] Phil. Trans., A, **192**, 499 (1899).

[4] Ann. Physik, **35**, 401 (1911).

	Mobility
Negative ion	26.0 cm./sec.
Positive ion, Li, Na, K, Rb, Cs	7.2 cm./sec.
Positive ion, Ba, Sr, Ca	3.8 cm./sec.

The experiments of Gold,[1] Wilson,[2] etc., leave no question but that at high temperatures the negative ion is the electron. The problem as to the nature of the positive ion is much more difficult. Marx[3] obtained mobilities of about 250, while Moreau[4] deduced a value of about 80 at 2000° C.

Experiments have been made by Moreau[5] to determine the mass and charge of the negative ion and its rate of diffusion through sheets of metal. The value of the mass obtained is between that of the corpuscle and the hydrogen atom. It is probable that the negative ion exists part of the time as a negative electron, and part of the time as a negative electron combined with one or more molecules. Negative ions diffuse very rapidly through sheets of metal, the sheets of metal playing the same role towards ions as a porous wall does towards a gas. The phenomena obey the law of Graham. A metal sheet in this case plays the role of a semipermeable membrane, it being permeable only to negative ions. By using these sheets to determine the mass of the negative ion, knowing its coefficient of diffusion, Moreau obtains a value for the charge of the negative electron which is 4.2×10^{-10}, agreeing well with the other measurements of this quantity.

Lusby[6] measures the current between electrodes placed horizontally, one above the other, in the flame, the upper plate being positive. A bead of salt is then placed in the flame just beneath the upper electrode. When the potential difference is great enough to drive back the positive ions against the uprush of the gas, the current suddenly increases. Knowing this critical voltage, the minimum electric force in the flame can be determined, and, knowing the velocity of the flame, the ionic mobility is obtained.

The following table gives the saturation current in a pure Bunsen flame between electrodes 3 cm. apart. The values are for the total current between the electrodes whose effec-

[1] P. Roy. Soc., A, **79** (1907).

[2] *Ibid.*, A, **82**, (1909).

[3] Ann. Physik, **2**, 790 (1900).

[4] Ann. chim. phys., **1903**.

[5] *Ibid.*, **18**, 433 (1909).

[6] Phil. Mag., **22**, 775 (1911).

tive area was 2 sq. cm. The relation between the temperature and the logarithm of the current is practically a linear one:

Absolute temperature	Saturation current
1150° C.	35×10^{-9} Amp.
1220° C.	51
1300° C.	107
1370° C.	150
1450° C.	230
1700° C.	600
1950° C.	1500

The potential gradients, as obtained by Lusby,[1] are given in the following table: This shows (1) a small anode fall; (2) a region of small constant electric force where the quantities necessary for a determination of the mobility are obtained; (3) a sudden cathode drop. The form of the several curves plotted from these data show the effect of change of temperature.

Mobilities of Positive Ions

(*a*) Monovalent metals (*b*) Divalent metals

Absolute temperature		Minimum E volts/cm.	Gas velocity		$K+$ mobility	$K_1\sqrt{\theta}$
1950		0.61	214		350.0	100.0
1700		0.65	210		320.0	93.0
1450		0.71	206		290.0	86.0
1370		1.58	181		115.0	83.5
1300		3.87	164		42.5	81.5
1220	(*a*)	7.18	183	(*a*)	25.5	79.0
	(*b*)	9.16		(*b*)	20.5	
1150	(*a*)	17.0	207	(*a*)	12.2	77.0
	(*b*)	3.3		(*b*)	6.2	

Metallic particles may be introduced into flames, and the electrification can be studied by means of exploring electrodes charged to a high potential (as, for instance, by means of a friction electrical machine). Metallic vapors are electropositive in the inner cone of a Bunsen flame, and are partially or wholly neutralized in the outer cone (as is lithium). Sodium, potassium and rubidium are only partly neutralized, while caesium remains strongly positive. According to Irving,[2] the principal series lines are emitted by regions of the metallic vapor that are either positive or neutral.

[1] P. Camb. Phil. Soc., **1**, 26 (1910).

[2] Physic. Rev., **29**, 243 (1909).

Flames are sometimes used for the rectification of high-tension alternating currents. If two electrodes, one of which is very small with respect to the other, be placed in a flame without solid matter in suspension and connected to a high-voltage alternating current, the current which passes will be unidirectional and will flow from the large to the small electrode. The effect is increased, according to Cathiard,[1] if the small electrode consists of fine points. He obtained a slightly luminous arc under these conditions, the point of which made a moving contact with the large positive electrode. Hydrogen, alcohol and illuminating gas flames gave the above effect. The small electrode consisted of a cylindrical carbon ring about 5 mm. in diameter. With voltages of from 2000 to 10,000 at 40 cycles and an electrode distance of about 8 mm., a current of 0.03 ampere was obtained. Above this voltage arcing took place and no rectification was obtained. Oscillograph examinations show the effect is due to a disintegration of the cathode.

Ionization and Chemical Action

Many chemists and physicists had noticed various electrical effects during chemical reactions, but very little of any importance was known until the theory of the ionization of gases was advanced. Among the early workers along this line was Townsend,[2] who showed that the ionized gas produced by the action of sulphuric acid on iron retained its electrification after passing through tubes of packed glass wool, thus proving that the electrification was not carried by coarse spray. Townsend found that the chlorine liberated by the action of hydrochloric acid on manganese dioxide is positively electrified, as is also oxygen produced by heating potassium permanganate.

Kosters[3] and Townsend have shown that many gases liberated in electrolysis are charged. The former attributes many of the results to the bubbling of the gases through the electrolyte. For example, hydrogen given off by the electrolysis of sulphuric acid at 40° or 50° has a considerable positive charge, whereas the charge of the oxygen is very small. When these gases are evolved from a solution of caustic potash, the hydrogen is but slightly electrified whereas the oxygen possesses a large negative charge which increases as the temperature is raised.

Townsend[4] found that the electrified gases had the power of producing clouds if they entered a vessel containing water vapor, although the air was not saturated with water vapor and the temperature was not lowered. H. A. Wilson[1] has shown that the spray from solutions of salts or acids, of sugar or glycerol, when filtered through sulphuric acid and passed into a damp atmosphere, produce a cloud.

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[1] Compt. rend., **146**, 20, 229 (1908).

[2] P. Camb. Phil. Soc., **9**, 345 (1988); Phil. Mag., [5] **45**, 125 (1908).

[3] Ann. Physik, **69**, 12 (1899).

[4] P. Camb. Phil. Soc., **9**, 345 (1897).

Although the sulphuric acid may rob the drops of water, still the neutral center of salt probably passes on, and when it enters into the damp atmosphere, the water condenses about the salt and forms a drop of solution. As the vapor pressure for these solutions is smaller than for pure water, they do not evaporate, although the gas is not saturated with water vapor.

Bloch[2] has measured the mobility of the ions formed when hydrogen is produced by treating zinc with hydrochloric acid, when carbon dioxide is produced by treating marble with hydrochloric acid and when oxygen is generated by heating potassium permanganate. His value was about 0.001 cm. per second, and, assuming Stokes' law, his value for the radius of the ions is 2.5×10^{-7}.

The ionization of air and other gases passed over phosphorus has been studied by Barus,[3] Schmidt,[4] Harms,[5] Bloch[6] and others. Barus found that hydrogen passed over phosphorus is not ionized. Bloch has shown that the mobility of the ions is about 0.001 cm. per second, the radius being about 10^{-6} cm. and the coefficient of recombination about a thousandth that of the ions produced by X-rays. The ions seem to consist of oxides of phosphorus condensed about the ordinary small ions.

Elster and Geitel[7] have shown that air passed over hot sulphur, even at a very high temperature, is not ionized.

Becker[8] considers that the size of nuclei in a gas containing ozone and a vapor such as ammonia depends on the concentration of the ozone and of the vapor.

Le Bon,[9] Miss Gates,[10] and Kalahne[11] have shown that the hydration and dehydration of certain salts (quinine sulphate) is accompanied by ionization. Driving off the water of crystallization from many salts by heating is usually accompanied by ionization.

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[1] Phil. Mag., [5] **46**, 454 (1898).

[2] Ann. chim. phys., [8] **4**, 25 (1906).

[3] Experiments with ionized air, Washington, 1901.

[4] Ann. Physik, **10**, 704 (1903).

[5] Physik. Z., **4**, 111 (1902).

[6] Ann. chim. phys., [8] **4**, 25 (1905).

[7] Ann. Physik, **39**, 321 (1890).

[8] *Ibid.*, **36**, 215 (1911).

[9] Compt. rend., **130**, 891 (1900).

[10] Physic. Rev., **18**, 135 (1904).

[11] Ann. Physik, **18**, 450 (1905).

Beattie[1] and Garrett and Willows[2] have mixed sodium chloride and iodine together on a plate, and heated the mixture to about 300°. The result is an emission of large numbers of positive and a smaller number of negative ions by the salt. The latter investigators find that by heating zinc chloride or iodide, in platinum vessels to 350°, large quantitites of ions are given off, and as the temperature is raised, the number of emitted ions is increased. If the zinc iodide was kept at a constant temperature, the rate of emission of ions diminished as an exponential function of the time, and at 360° the rate of production of ions fell to half value in 41 minutes. The mobility was 0.0017 cm. per second. Many salts heated to redness give off more ions than the corresponding metals would do, and the excess ions may be either positive or negative, according to the nature of the salt.

Under some conditions it seems that chemical reactions may be accompanied by the emission of electrons. Haber and Just[3] claim that the action of phosgene on clean sodium-potassium (caesium, potassium or lithium) surfaces in the dark at ordinary temperatures and in high vacua is accompanied by the emission of electrons. Bromine acts in the same way as phosgene.

Broglie and Brizard[4] conclude from a series of experiments that chemical action itself is not accompanied by any ionization in the surrounding gas. They would explain the ionization in the neighborhood of a chemical reaction as being due to heating (incandescent metals and metallic oxides emit ions; and silver[5] produces ions at as low a temperature as 200°), by the formation and breaking of bubbles, or by the decrepitation of crystals, etc. The following table gives a summary of the results obtained for various chemical reactions:

A. The fumes produced in moist air by phosphorus trichloride and pentachloride, arsenic trichloride, stannic chloride, antimony pentachloride, silicon fluoride, hydrochloric acid, hydrobromic acid, fuming nitric acid, fuming sulphuric acid, anhydrous sulphuric acid, ammonia gas in the presence of chlorine, hydrochloric acid gas, nitric acid gas or ozone do not produce charged particles. When exposed to the rays from radium, many of the particles are given a unit charge. In

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[1] Phil. Mag., **48**, 97 (1899); **11**, 422 (1901).

[2] *Ibid.*, **8**, 437 (1904).

[3] Ann. Physik, **36**, 308 (1911).

[4] Le Radium, **7**, 164 (1910).

[5] Strutt: Phil. Mag., **1902**, 98.

A. Reactions without the breaking of a liquid surface	Reactions between gases at low temperatures	No conductivity
	Double decomposition. Formation of precipitates in a liquid	No conductivity
	Dry decomposition	No conductivity
B and C. Reactions involving the breaking of a surface	Breaking of an inactive surface by bubbling	No conductivity
	Gas prepared by the wet way	Conductivity
	Rapid reactions, a chemical being put into water	Conductivity
	Gases prepared with the decrepitation of crystals	Conductivity
	Oxidation of sodium in wet air	Weak conductivity
D. Reactions accompanied wth incandescence	Rapid combustion	Conductivity
	Metals in oxygen, chlorine, etc.	Conductivity
	Flames	Conductivity
E. Reactions accompanied with luminescence	Oxidation of phosphorus	Conductivity
	Phosphorescence of sulphur and arsenic	No conductivity
	Phosphorescence of sulphate of quinine	Conductivity

warming gently substances like calcium acetate, lead oxide, carbonate of lead, and oxide of mercury, the finely divided particles given off are neutral. It is true that silver oxide gives off charged particles, but these are probably from the silver atoms.

B. Concentrated nitric acid in contact with benzene, the essence of turpentine, etc., produces a very violent reaction accompanied with the evolution of gas which is neutral, thus showing that in the case of a liquid that does not produce ionization by bubbling, there is no ionization in the gases evolved from at least some chemical reactions.

The formation of ozone by the oxidation of phosphorus seems to be closely related to its ionization and phosphorescence, although the ozone[1] can be absorbed without removing the ionization. The phosphorescence can be removed several meters from the phosphorus, according to Bloch.[2] The oxidation of phosphorus to phosphoric anhydride is without ionization; the oxidation of the anhydride is accompanied by intense ionization. Sulphur at 200° shows phosphorescence and liberates ozone even without ionization. Flames of the thiosulfocarbonic ester, $H_3CSCSOCH_3$, sulfocarbamic ester, $H_3COCSN(CH_3)_2$, and sulfocarbonic ester, $CS(OCH_3)_2$, burn without any accompanying ionization.

Ions of Small Mobility

The ions produced by most of the ionizing radiations possess mobilities of about a centimeter per second, the negative ions usually having a slightly greater mobility. These ions are usually considered as consisting of aggregates (the size depending upon conditions) of gaseous molecules, to or from which one or more electrons have been added or removed. It may be that the ionizing radiation has broken some of the molecules into charged ions, and around these, as nuclei, a cluster of molecules has formed. One might call the ions having a mobility of about 1 cm. per second, small ions. It is these ions that are produced by α-, β-, γ- and X-rays, in the photoelectric effect, by cathode rays, canal rays, etc.

There are other examples of gaseous conductivity, however, in which the ions produced have much smaller mobilities. Bloch[3] has measured the mobility of ions produced when hydrogen is generated by the action of hydrochloric acid on zinc, when carbonic acid gas is made by treating marble with hydrochloric acid, and when oxygen is prepared by heating potassium permanganate. The mobility was found to be about 0.001 cm. per second.

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[1] Physik. Z., **4**, 102 (1903).

[2] Ann. chim. phys., **22** (Apr., 1911).

[3] *Ibid.*, **4**, 25 (1905).

The ions present in a gas that has been bubbled through a liquid have mobilities ranging from those of small ions to those of large ions. The mobility of the ions has a mean value that depends on the nature of the liquid. For pure water the mobilities of both ions are about 0.2 cm. In passing gradually from water to pure sulphuric acid the mobilities of the ions decrease gradually to about 0.0002 cm., this being the mobility of the large ions.

The electrification produced by spraying seems to be produced in the same manner as that by bubbling. The electrification produced by gases prepared by the wet way is due to the presence of charged and neutral centers that seem to be formed in exactly the same way as ions and neutral centers are formed by bubbling. Chemical reactions that take place in the dry way are not accompanied by ionization.

When dust-free air is acted upon by ultraviolet light, Sachs[1] finds ions of small mobility. Air, carbon dioxide, oxygen and nitrogen are found to contain uncharged nuclei.

The most generally accepted hypothesis is to attribute to each ion the same electric charge, and consider the differences of the mobilities to be due to differences in the masses of the material centers. In order to determine the dimensions of these ions, one usually makes use of the law of Stokes: where a is the radius of the particle falling through a medium of viscosity, μ, d is the density of the medium, D the density of the falling particle, v its velocity, and g the value of gravity,

$$4/3\pi a^3 g(D - d) = 6\pi a v \mu.$$

This formula, according to the results of Perrin, seems to hold for particles, the radius of which is as small as 0.1μ. Letting the density be unity, then ions having a mobility of about 0.001 cm. would have a diameter of about $10\mu\mu$. This value is of about the same order as that found by other methods. The limiting thickness, for instance, of a film of oil on water, according to Rayleigh, Schuke, Röntgen, and Fisher, is of the order of several $\mu\mu$. The same bulk is found for solid pellicules which form on the surfaces of liquids (Melsens, Ramsden, Devaux, Metcalf) and for the walls of soap bubbles according to Bleateau, Drude, Reinold and Rucher. The thickness of the black spot of liquid films, which is the smallest thickness that is allowed by the cohesion of the membrane, and which seems to consist of two superficial layers and a central portion, is several $\mu\mu$. Beyond this limit of thickness the ordinary properties of matter would disappear. The molecular diameter is about $0.1\mu\mu$. It would follow then that the smallest drops would contain about 10^6 molecules. Particles of a similar nature are formed when air is passed over phosphorus, in the cooled gases about flames, or in bubbling and the breaking of drops (*ecrasement*), etc. The ions are probably produced by chemical action in the first case, and in the other cases they may be formed at the expense of electrolytic ions, or from the formation of the double layer.

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[1] Ann. Physik, **34**, 469 (1911).

The Charging of Neutral Centers and Their Properties

There are many conditions in which one can imagine the existence of small neutral particles, relatively large compared with molecules and small ions. These centers will attract the ions, and will combine with them to form large ions. Suppose that a gas contains M neutral centers per cc. (the ions having been removed by passing the gas through a charged condenser), and that it is then subjected to an ionizing radiation that will produce p positive and n negative small ions per cc. When equilibrium is reached (which may require a considerable length of time) let there be P positive and N negative "large" ions per cc. When there is equilibrium, it will be supposed that the number of recombinations of neutral centers and of small ions is the same as the rate of disappearance of large ions (dP/dt).

$$dP = A[M - (P + N)]p \qquad (1)$$

A is the coefficient of recombination of the small positive ions and the neutral centers, the rate of recombination being assumed to be proportional to the product of the numbers present. A will depend on the mobilities of the neutral centers and small positive ions. Equation (1) gives the increase of (P). The decrease of P is due to a recombination of large positive ions and large negative ions, and of large positive ions and small negative ions and is:

$$dP = \alpha PN + BPn \qquad (2)$$

For equilibrium,

$$A[M-(P + N)]p = \alpha PN + BPn \qquad (3)$$

Here α, the coefficient of recombination of large ions, will be very small compared with B, the coefficient of recombination of large and small ions. If we asssme that the coefficient of recombination is proportional to the sum of the mobilities of the two kinds of ions considered, then we may neglect the term αPN in Equation (3), especially as n is quite large.

For positive ions, then,

$$M - (P + N) = BP/A \qquad (4)$$

For negative ions,

$$M - (P + N) = B'N/A' \qquad (5)$$

These equations are independent of p and n, showing that the number of large ions is independent of the ionizing radiation if this is of sufficient intensity and depends only on the number of neutral centers present, and certain constants. P/M and N/M are functions of A, A', B, and B', which are in turn functions of the mobilities, and they have a value of about 0.1.

Subtracting (4) from (5), $P/N = AB'/A'B$.

If k_+ or A is the mobility of the small positive ions,

k_- or A' is the mobility of the small negative ions,

K is the mobility of the large ions, then $B = K + k_-$ and $B' = K + k_+$

$P/N = AB'/A'B = k_+(K + k_+)/k_-(K + k_-) = k_+^2/k_-^2$ approximately. Since k_- is greater than k_+, there should be a considerable excess of large negative ions over large positive ions.

Quite an extended investigation has been made by Broglie[1] upon ions of small mobility produced in various ways. To obtain the ions produced by chemical action he passed a mixture of carefully purified air and a small amount of hydrogen through a heated glazed tube, and then into his cylindrical condenser used for measuring the mobilities. (The water formed in this way indicated the presence of hydrogen dioxide.) Currents of hydrogen mixed with small quantities of air have given exactly analogous results. (Currents of hydrogen passed through copper oxide did not show any ionization, but this may have been due to loss of the ions by diffusion.) The intensity of the ionization depended very much upon the way the tube in which the chemical reaction took place was heated. The mobility of the ions is much less than that of the small ions, but greater than that of the ions from flames. The mobility is found to decrease as the proportion of hydrogen is increased, and may be explained by supposing that the neutral centers are larger, the greater the amount of water condensed.

In the case of a chemical reaction in which there is no condensation, as in a carbon monoxide flame, no neutral centers would be formed, and therefore no large ions. Broglie has found that the mobility of ions from such a flame was about 0.05 cm. and was independent of the proportion of carbon monoxide. When the heated tube through which the air

[1] Ann. chim. phys., **16**, 1–69 (1909).

and carbon monoxide flow is free from any volatile substances, and the gases are thoroughly dry, there is no indication of a stable conductivity. Even in the case of a flame of carbon monoxide there is no indication of any conductivity when the entering gases are carefully purified.

If, however, the air admitted contains a little moisture, or the carbon monoxide a small amount of hydrogen, there is a large conductivity due to the presence of large ions. By heating a moist porous body at varying distances from the carbon monoxide flame, it is found that large ions are produced only when the source of neutral centers is close to the flame, thus indicating that in the flame there are produced small ions that possess a very large coefficient of recombination, similar to those produced by X-rays given off by radium.

It is possible to produce large ions in moist filtered air without any ionizing agent by passing it through a porcelain tube containing pumice stone heated to a dull redness. In this case the large ions are probably due to the dissociation of the water vapor.

In the formation of large ions in the cases above cited, it seems necessary to have present neutral centers; and these neutral centers are not always present in a gas containing water vapor. Broglie has shown this by warming a flask containing water and exposed to a tube of radium. Large ions are not produced in a gas made to pass through the flask of water until all the water has evaporated, and the flask is heated to 200° or 300°.

Broglie has found that neutral centers are easily filtered from a gas by passing the gas through cotton. They are destroyed when the gas is heated to a temperature greater than 250°. When a gas is removed from a flame, the number of ions gradually decreases. At the same time, the number of neutral centers also decreases, and apparently at about the same rate as the large ions. The proportion of large ions to neutral centers, $(P + N)/M$, is very small.

In 1894 Lord Kelvin[1] showed that air bubbled through water was charged negatively. This charge was decreased when salts or acids were added to the water, and in some cases the ionization of the air was reversed. In 1894, Thomson[2] showed that the presence of infinitesimal amounts of impurities in the water (such as rosaniline, for example) had a very great effect upon the ionization.

Kösters,[3] in 1900, showed that when 0.007 part of sulphuric acid per 100 of water was used, the air that bubbled through the solution was neutral. If the amount of acid was greater, the air was positive; if less, the air was negatively charged.

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[1] P. Roy. Soc., **57**, 335 (1894).

[2] Phil. Mag., **37**, 341 (1894).

[3] Ann. Physik, **69**, 12 (1899).

Lenard,[1] having his attention drawn to the exceptional atmospheric electrical phenomena about waterfalls, examined the effect of water splashing against a plate, and found that the water becomes positively charged and the surrounding air negatively charged. He found the effect to depend largely on the purity of the water, and in the case of a weak solution of sodium chloride, he noticed that the air was positively electrified. Lenard shook mercury in a bottle, and found the air negatively charged. Turpentine, in being sprayed, became negatively electrified and made the air positive, the effect being the opposite of that of water. Carbon bisulphide gave the same effect as water. In the case of water, the presence of hydrogen caused the amount of electrification to be much smaller. Kähler's[2] work indicates that in bubbling through pure water, only negative ions are formed in the air, whereas when salts are present both kinds of ions are formed. Aselmann[3] finds that the mobility of ions in air made by splashing pure water varies from 4 cm./sec. to 0.00027 cm. per second, the mobility of the greater number of ions being from 4 cm. to 0.016 cm. per second. For a 0.2 per cent. solution of sodium chloride, the mobilities of the negative ions ranged between 4 cm. to 0.0019 cm. per second, while the mobilities of the positive ions were between 0.088 and 0.0006 cm. per second. Pacini[4] has studied the ionization produced by bubbling in water containing a trace of coloring matter. Solutions containing eosin, resorcinol, etc., communicate to a gas a charge that is independent of the concentration, whereas rosaniline, fuchsine, etc., produce an ionization whose sign is variable. Bloch[5] gives the mobility of the negative ion produced in air bubbled through pure water as 0.115 cm. per second, and 0.08 cm. per second for the positive ion. For sulphuric acid, the mobility is about 0.0003 cm. per second. A thorough investigation has been made by Broglie,[6] and some of his results will now be given.

The phenomena are very complex, the ionization in the gas depending upon the chemical nature and condition of the gas, the nature and temperature of the liquid, the form of the orifice from which the bubbles are produced, the distance of the orifice below the surface of the liquid, and the amount of pressure under which the gas issues from the orifice.

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[1] Ann. Physik, **1892**, 584.

[2] *Ibid.*, **12**, 1119 (1903).

[3] *Ibid.*, **9**, 960 (1905).

[4] Atti accad. Lincei, **1904**.

[5] Compt. rend., July 1, **1907**.

[6] Ann. chim. phys., **16**, 42 (1909).

As the pressure of the gas is increased at the orifice where the bubbles are formed, the intensity of the ionization is very small until the pressure reaches about 9 cm. of mercury, and then it rises very rapidly and is approximately proportional to the pressure. Using the same size of orifice, the intensity of ionization is much greater for an alcoholic solution. Increasing the size of orifice from 0.15 mm. to 0.35 mm. also increases the ionization.

Starting with pure water, the ionization is measured for solutions containing varying amounts of a large number of salts and acids (sodium, potassium and barium chlorides, potassium bromide and iodide, hydrochloric, sulphuric and acetic acids, potassium hydroxide). Curves are plotted between the intensity of (positive) ionization and concentration. The ionization, small at first, in general rises rapidly to a maximum at about 0.0015 normal, and then decreases slowly. The curve for the negative ions starts with a considerable value, attains a maximum for a concentration of about 0.005, and then descends. It cuts the curve for the positive ions at about 0.01 normal concentration, remains for a long distance in the same region, and then falls for the strong concentrations. The total charge would be represented by a difference in the ordinates of the two curves. As the form of the curve does not vary when the bubbling is done at different depths in the liquid, it would seem that recombination does not influence the results.

The curve representing the ionization resulting from a solution of alcohol or ether in water is very different from the effect produced by the addition of a salt. An example is the following:

KCl in water	Conductivity	Alcohol in water	Conductivity
0	100	0	100
N/152000	134	N/152000	104
N/38500	229	N/38500	113
N/4000	422	N/4000	116

In general, air bubbled through methyl and ethyl alcohols, ether, acetone, aldehyde, pure sulphuric acid and aniline contains ions, while air bubbled through benzene, toluene, xylene, carbon bisulphide, carbon tetrachloride, pentane, hexane, chloroform, the essence of turpentine, liquid air, etc., produces only neutral centers that can be ionized by the rays from radium. The two classes of liquids have very little in common. Broglie believes that there may be some connection between the power of the first group of liquids to absorb oxygen and the electrical effects produced by bubbling. Mercury produces neither ions nor neutral centers, and so does not belong to either of the above classes. The ionizing effect produced when mercury is shaken in a vessel must be of a different nature from that produced by other liquids. Pure glycerol and oil of vaselin give neither ions nor neutral centers.

The phenomena observed when oxygen or hydrogen are used instead of air are essentially the same, although in the case of hydrogen the mobilities of the ions are somewhat greater.

In the case of liquids of the first class, it is found that an exposure to X or radium rays actually reduces the ionization, and in an example given by Broglie this decrease amounted to about 85 per cent.

Bloch[1] finds that if a little olive oil, benzene, petroleum, vaselin, turpentine, etc., is poured over the surface of a liquid in which a gas is being produced by the wet way, no ionization results. This layer of oil can be made very thin if the gas evolved consists of very small bubbles. These results, with the work of others, might then be taken to indicate that the ionization by bubbling, the Lenard effect (ionization due to the falling or splashing of drops), and the ionization produced by chemical reactions, are all due to a common cause. For instance, bubbling is usually, if not always, accompanied by the formation of a fine mist, so that the accompanying ionization may simply be a Lenard effect. This view is supported by the fact that the ionization effect for fine spray of a liquid is the same as that produced by bubbling.

The ions produced by bubbling possess varying mobilities, the ions from sulphuric acid being "large," whereas those formed by the bubbling of pure water are small. The ions produced during chemical reactions also have varying mobilities. Bloch has used the surface of a liquid in which chemical reactions are taking place as one of the plates of a condenser from which he measured the saturation curves. These "static saturation" curves are found to be straight lines that keep on ascending to at least a field strength of 1100, which is as far as Bloch worked. The curves are the same for positive and for negative ions, and are similar to those found by Miss Gates[2] for the ionization from sulphate of quinine.

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[1] Le Radium, 7, 354 (1910).

[2] Physic. Rev., 18, 146.

Bloch considers that the curves are due to the production of ions and neutral particles, and that the latter may become charged in an electric field and play a more important role than the ions. In chemical reactions these neutral particles, or liquid dust, often become charged, and they can then be distinguished from ions, since their charges and their mobilities are a function of the electric field in which they are formed. The neutral particles of Bloch are very similar to the neutral centers studied by Broglie and others, although there are some differences. Bloch, for instance, finds the neutral centers in hydrogen do not become charged when exposed to the rays from radium, whereas Broglie finds that under such circumstances the neutral centers become large ions. Broglie finds neutral centers from the bubbling of inactive liquids such as benzene, and does not obtain them for water. Bloch finds them, however, for solutions that are "active," by bubbling. Broglie's neutral centers are visible in the ultramicroscope, whereas those found by Bloch in hydrogen are not, being too small to appear optically.

Charging these neutral particles by the action of an electric field, and letting e', K', D' and r be the charge, the mobility, the coefficient of diffusion and the radius of the ions, we have

$$K'/D' = Ne'$$

$$e' = 6\pi\mu r K' \text{ (Stokes' law)}$$

K' is found to be 0.19 cm. per second. By using Townsend's method,[1] the coefficient of diffusion was found to be $D' = 0.0017$. Using $K = 1.16$, and $D = 0.035$, $e'/e = 2.5$, the value e' being a mean one. Broglie's large ions often have a charge of 30 to $50e$.

Electrolytic oxygen from potassium hydroxide and sulphuric acid solutions contain charged mist nuclei. The charges on these nuclei are e, $2e$ and $4e$, according to Lattey.[2]

Ehrenhaft[3] has investigated, by the ultramicroscopic method, the charge of isolated particles produced by arcs of gold, silver and platinum. The method was to measure the velocity of the fall of the particles in the presence of an electric field, and then in absence of the field. The particles were found to be spherical and metallic, and certainly were of sufficient size for Stokes' law to apply. The work was done in a dry gas for the reason that in the presence of moisture the particles showed a very marked Brownian movement similar to that of particles of phosphorus fumes.

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[1] Conduction of Electricity, p. 420.

[2] Phil. Mag., **18**, 26 (1909).

[3] Physik. Z., **11**, 619 (1910).

For phosphorus, *e* varied from 0.52 to 28.90 × 10^{-10}; for gold, from 0.53 to 7.18 × 10^{-10}; for silver, from 0.94 to 26.65 × 10^{-10}; and for platinum, from 1.5 to 12.43 × 10^{-10}. A large number of measurements led to values much less than the classic value 4 × 10^{-10}. Efforts to find statistical groupings of the value of *e* were unsuccessful, so that it is concluded that there exist electric charges that are much smaller than the charge on the electron.

Humidity influences positive and negative ions in such a way that the negative ions act more easily as nuclei for the condensation of water vapor. It might be expected, therefore, that any damp ionized gas that is dried by being passed through a tube plunged in liquid air would show an excess of positive ions. Lusby[1] does not find this to be the case, although he finds that the dried air possesses from two to three times as many ions. In his experiments, the ionizing agent consisted of uranium oxide. Lusby considers that this effect is not due to diffusion, because it is independent of the size of the tubes; and that it is not due to a variation in the number of large and small ions, because the effect is the same when only small ions are present. Recombination should not produce such an effect, since Erkson has found that the coefficient of recombination increases as the temperature decreases. The large increase in ionization after passing through liquid air is found to occur for dry air, and is therefore not dependent on moisture.

Mme. Curie[2] has shown that the presence of radium emanation causes the condensation of certain vapors in the form of a persistent mist that can be seen in the light of an electric arc. The condensation centers are probably particles of the induced radioactivity that are suspended in the gas and the mist is probably due either to the action of electrostatic attraction or chemical affinity. The radium emanation causes a feeble mist for several days in the presence of pure water and air. In carbon dioxide and water no mist is formed, but if some sulphuric acid is present a mist is formed. The condensation centers in the above cases may be nitrogen compounds and particles of sulphuric anhydride formed during the decay of the radium emanation. Persistent and thick mists are formed with iodine in carbon dioxide, and camphor in air.

Molecular Aggregates Produced in Gases by Sudden Cooling

Owen and Hughes[3] describe experiments that show that certain gases when suddenly cooled contain a large number of charged nuclei which act as centers for the condensation of supersaturated water vapor. The temperature below which it is necessary to cool the gas, in order that these nuclei be formed, is designated as the nucleating temperature. The nucleating temperature is found to depend to some extent upon the rate at which the gas is cooled, and upon the dimensions of the vessel used.

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[1] P. Camb. Phil. Soc., **15**, 459 (1910).

[2] Compt. rend., **147**, 379 (1908).

[3] Phil. Mag., Oct., **1907**, p. 746; June, **1908**. Owen: *Ibid.*, Oct., **1911.**

It was found that many gases differ from air. In air and similar gases, it is possible that aggregations of the slowly moving molecules are formed, a sort of incipient liquefaction. The number of these molecular aggregates, for some unexplained reason, is much larger if the cooling is sudden. The rapid disappearance of the nuclei at higher temperatures is probably due to the more vigorous bombardment by the more rapidly moving gas molecules.

Air containing these nuclei, when left to stand for twenty or thirty minutes, is found to be practically free of them. For dusty air, however, these nuclei are much more persistent, as they also are at low temperatures.

No nuclei are formed in carbon dioxide, ethylene, methane, etc., by cooling until the temperature of condensation is reached. When condensed carbon dioxide is allowed to sublime, nuclei are formed, indicating that aggregates as well as separate molecules escape; on the other hand, the gases from liquid air, oxygen, ethylene and methane are free of nuclei, indicating that the evaporation of a liquid consists in the escape of separate molecules.

C. Barus[1] and Owen and Pealing[2] have not obtained any evidence for the existence of nuclei in air blown over camphor, naphthalene or benzoic acid. Owen and Pealing obtained quite marked effects, however, with iodine in moist air and oxygen. They found that the effects are very persistent, and are only produced by the action of light. The nuclei seem to be quite small, and apparently grow to their maximum size after the light has acted for about a second. The nuclei all disappear about a minute after the light has been screened off.

The iodine nuclei are uncharged, and are only effective when the expansions take place in supersaturated water vapor in the presence of light. The effect seems to be photochemical in character, and probably belongs to the class of phenomena studied by Tyndall,[3] Aitken[4] and C. T. R. Wilson.[5] Tyndall found that ultraviolet light caused clouds to form without ex-

[1] "Condensation of Vapor as Induced by Nuclei and Ions," Carnegie Institution of Washington, May, 1907.

[2] Phil. Mag., **21**, 466 (1911).

[3] Phil. Trans., **160**, 333 (1870).

[4] P. Roy. Soc. Edinb., **39**, 15 (1897).

[5] Phil. Trans., **192**, 403 (1899).

pansion in air containing traces of amyl nitrite, iodide of allyl and other vapors. Aitken found that clouds are produced in ammonia, sulphurous acid, hydrogen sulphide, hydrochloric acid and chlorine, when expanded after exposure to sunlight. Wilson found that moist air or oxygen, when exposed to intense ultraviolet light, produced condensation nuclei on which clouds could be obtained without any expansion at all. Wilson has suggested that this cloud formation is due to the formation of hydrogen peroxide. Bevan,[1] in his experiments on the combination of hydrogen and chlorine under the influence of light, found that some substance is produced by the action of light on chlorine and water vapor that acts like condensation nuclei, and that the formation of these nuclei is necessary for the production of hydrochloric acid.

The iodine nuclei are not produced after the iodine has been in the apparatus for a few days, but reappears as soon as the glass walls of the apparatus are rinsed with water. The passage of the iodine vapor facilitates the formation of the nuclei very greatly.

In experiments upon condensation nuclei it is very important to eliminate the effect of impurities. Lenard[2] and Wolf showed that the uncharged nuclei are often present in a gas and that these are copiously formed by the action of ultraviolet light. These nuclei are unaffected by cooling but are destroyed when heated to about 180°. Their diameter appears to be twenty or thirty times that of gas molecules and they are probably products of chemical reactions.

Ionization in Sprays

Allesandrini,[3] Wilson,[4] Eve,[5] Pomeroy,[6] and many others have studied the ionization produced by the fine spray of water. The relative number of negative to positive ions was found by Eve to be in the ratio of 4 to 3. Both positive and negative ions are removed by filters of glass wool (6.5 cm. thick). Such a filter can be used as a "Faraday box" to measure the total charge carried off by the air or spray. By this means it can be shown that a current of air and spray contains an excess of negative electrification. The heavier part of the spray that falls is charged positively. It also seems probable that most of the positive ions become attached to water drops while the negative ions do not seem to become so, easily attached. Evaporation does not seem to be accompanied by ionization, although, according to Holmgren,[1] ripples on a water surface produce ionization. Interesting experiments could be carried out by electrifying the nozzle and in passing the spray through various kinds of electrical discharges.

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[1] Phil. Trans., **202,** 347 (1903).

[2] Ann. chim. phys., **3,** (1889); Ann. Physik, **1900,** Nos. 1 and 2.

[3] Nuovo Cimento, **4,** 389 (1902).

[4] Phil. Mag., July, 1902.

[5] *Ibid.*, **1907,** 382.

[6] Physic. Rev., **27,** 492 (1908).

Lousdale[2] finds that the splashing of mercury on an iron plate produces a large excess of positive ions, and that a considerable portion of these ions have a small mobility. The amount of ionization depends upon the nature of the surface upon which the mercury is splashed. Becker[3] has measured the mobility of the ions produced by the fall of mercury in hydrogen and carbon dioxide, the mercury drops striking a solid obstacle. He finds that there is no definite value, but that there are ions of all mobilities. Immediately after their formation, the mobilities range between 0.96 and 0.015 cm. per second. After a short time large ions of a mobility of from 0.0062 to 0.0027 appear, and the number of these large ions continues to increase.

If a stream of water is directed vertically to a distance of several feet and then allowed to fall on a sheet of metal, the sound of the falling drops will be heard.[4] Bringing a charged body near the jet, where it breaks into drops, will result in the formation of larger drops and hence a sound of lower frequency. When the stream is small the drops are found to form in a line when charged, but scatter when uncharged, and it appears to be due to this fact that the charged drops tend to coalesce more as they go upwards. These phenomena hold only when the drops carry small charges. The coalescence of the charged drops is probably due to their being of quite different sizes.

The action between two spheres[5] charged with the same sign of electricity is not always one of repulsion. The force will be one of attraction in many cases, as shown by Burton and Wiegand, and this probably explains the coalescence of the charged drops. This attraction, combined with the Bjerknes effect, may play a considerable role in the aggregation of particles suspended in gases.

Seeliger[6] finds that falling water drops carry down but a small negative charge when they pass through air that is being ionized by X-rays. Great care must be taken to eliminate the "water-dropper" effect of the drops leaving the nozzle and the Lenard effect. The charge carried down by the drops is measurable only when the X-rays are acting. This is probably due to the air film about the drop being more strongly ionized, owing to secondary radiation from the drop.

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[1] Soc. Physiographique de London, 1894.

[2] Phil Mag., 20, 464 (1910).

[3] Ann. Physik, 31, 98 (1910).

[4] See various sections of Lord Rayleigh's papers. Burton and Wiegand: Phil. Mag., 23, 148 (1912).

[5] Collected papers of Lord Kelvin. Russel: Physic. Soc. London, 24, 22 (1911).

[6] Ann. Physik, 31, 500 (1910).

The Production of Nuclei

H. A. Wilson and others have shown that X- and γ-rays not only produce ions in a gas, but nuclei also. These nuclei can be detected in the production of a sudden expansion of the gas, by decreasing the pressure (δp), so that there is a supersaturation of the water vapor present; and if the expansion is sufficient, condensation of water vapor follows. Barus defines the fog limit as the amount of expansion (δp) necessary to cause dust-free air saturated with water vapor to condense so as to form clouds. A very extended study has been made by Barus[1] upon the coronas that are produced by fogs and clouds when a beam of light passes through them.

When nucleation and ionization are produced by the same process, the intensity of the two phenomena remains relatively about the same, both nuclei and ions being produced at the same rate. The subsequent life history of nuclei and ions, however, is quite different, nuclei being in general very fleeting. In some cases nucleation may be a result of ionization, though many cases are known of nucleation without any accompanying ionization.

The apparatus of Barus usually consisted of a long rectangular wooden condensation chamber having plate glass windows. A layer of water is kept in the bottom to keep the air saturated with water vapor. One end of the apparatus is exposed to an X-ray bulb and the other end is connected with an apparatus for producing sudden exhaustion.

A pressure difference is selected such that condensation just begins for dust-free air; and for the apparatus used the volume expansion was about 1.48. The number of nuclei range from 11,000 to 95,000 per cc. for dust-free filtered air. According to Barus, dust-free air contains large and small nuclei to the number of millions per cc., and these rapidly increase as the order of molecular size is approached. These nuclei Barus considers as a kind of colloidal air molecule.

While the phosphorescent, photographic and ionizing effects of an X-ray bulb decrease rapidly with the distance, the nucleating effect is nearly constant, according to Barus, over distances in some cases varying from six to six hundred cm., and the nucleating radiation is not stopped by lead screens several cm. thick when the fog chamber is not protected. When the fog chamber is surrounded with lead, and only a small window is left open, the nucleating power of the rays acts in the same manner as the ionizing power. When the nucleating effect is almost independent of the distance, it is probable that the effect is due to secondary X-rays.

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[1] Carl Barus: Smithsonian Contributions, Nos. 1373, 1903, Vol. 34, 1905. Science; Apr. 14, 1905. Publications Nos. 40 and 62, Carnegie Institution of Washington, etc.

There are several kinds of nuclei present in dust-free air. These Barus classifies as persistent, fleeting, and colloidal nuclei.

Ordinary dustlike or persistent nuclei can be separated from air by passing it through a cotton filter. These nuclei require the smallest amount of supersaturation of water vapor to produce condensation. As a rule, they consist of foreign bodies in the air, although they can be produced by X- and γ-rays that are of sufficient intensity. This kind of nuclei may persist for hours after the exciting radiation is removed, decaying to half value in ten minutes, and one-fifth value in eighty minutes. Their number keeps increasing for ten minutes or more after the exciting radiation is turned on.

Intermediate rates of generation and decay may be obtained by having the X-ray bulb of radium at varying distances from the fog chamber.

The second kind of nuclei vanish in a few seconds after the exciting radiation is removed. These are named fleeting nuclei, and for the production of corona they require an exhaustion almost approaching the value of the fog limit. They seem to be almost instantaneously generated—at least, in less than a second's time—by the radiation that produced them. On the removal of the radiation, they decay according to an exponential law, their number falling to half value in two seconds, and to one-fifth value in twenty seconds. If charged, these nuclei seem to be the ordinary ions. Their size seems to depend upon the kind of radiation by which they are produced. Fleeting nuclei pass continuously into persistent nuclei. When condensation takes place upon fleeting nuclei, about one-fourth of these nuclei become persistent nuclei upon the re-evaporation of the clouds formed. Barus thinks that all nuclei upon which there has been condensation become stable and persistent. These nuclei may be called solutional nuclei. If N is the number of these nuclei per unit volume and the source of nuclei is cut off the number of nuclei decrease so that

$$dN/dt = -\alpha N^2$$

where $\alpha = 0.002$.

According to Barus, colloidal nuclei are a structural part of a gas, and are always present. They are reproduced as rapidly as they are removed. Their number increases rapidly as their diameter decreases to that of molecular dimensions. Barus considers that the size of molecules varies in somewhat the same manner as the velocity is distributed amongst them. The number of colloidal nuclei is much greater than the number of ions, and increases rapidly as the size of the nuclei becomes smaller. Barus considers that the action of an external radiation or of an expansion is to cause a sort of flocculation of the colloidal nuclei. The presence of strong odors (camphor, naphthalene, turpentine, etc.) did not have any apparent effect in nucleation. (The exact nature of these odors does not seem, therefore, to be that of colloidal nuclei.) No diurnal variation was observed in the number of colloidal nuclei.

Barus[1] has done a little work on exhaustions in other gases than air, and also by using liquids other than water. He has found the number of nuclei to vary with the solvent, and with the solute dissolved in it. Thus he finds, for shaking, the value of N (number of nuclei per cc.) for pure water, 130; organic substances dissolved in water (sucrose, glucose, glycerol, urea, etc., 1 per cent. solution), $N = 600$; mineral salts dissolved in water (1 per cent. solution) (nitrates, chlorides, sulphates, etc.), $N = 1300$; naphthalene in benzene, $N = 3500$; paraffin in benzene, $N = 5000$. If the solvent is pure, the nuclei produced by shaking are very fleeting, and as the concentration increases for a given solvent, the persistence increases with the number of nuclei formed.

Positive Rays

Some very important discoveries have been made by J. J. Thomson on the value of the charge and the mass of ions in the "positive" rays of vacuum tubes. The measurements simply consist in obtaining the deflection of the rays by the action of magnetic and electric fields. In the positive rays ions of the following type have been found: $\overset{+}{H_2}$; $\overset{+}{H}$; $\overset{-}{H}$; $\overset{-}{O_2}$; $\overset{-}{O}$; $\overset{+}{C}$; $\overset{+}{CH_4}$; $\overset{-}{CN}$; $\overset{+}{He}$; $\overset{-}{Cl}$; $\overset{+}{H_3}$; $\overset{++}{He}$; $\overset{++}{C}$; $\overset{++}{N}$; $\overset{+}{He_3}$; $\overset{+}{O}$; $\overset{+}{CN}$; $\overset{+}{C_3}$; $\overset{+}{O_3}$; $\overset{+}{C_6}$(?); $\overset{+}{O_6}$; $\overset{++}{Hg}$; $\overset{+}{Hg}$; $\overset{+}{Hg_4}$; $\overset{++}{O}$; $\overset{+}{N}$; $\overset{+}{N_2}$; $\overset{+++}{N}$; $\overset{+++++}{Kr}$; $\overset{+++}{N}$; $\overset{+}{Ar}$; $\overset{++}{Ar}$; $\overset{+++}{Ar}$; $\overset{-}{C}$; $\overset{-}{S}$; $\overset{-}{Cl}$, etc. This method has proven valuable in analyzing small quantities of gas and by its use Thomson believes that he has discovered several new elements.

Up to the present time the method has not been applied to the determination of the exact nature of chemical reactions.

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[1] Am. J. Sci., **33**, 107 (1912).

One of the difficulties of an application is the temporary nature of many of the ions of any given kind of ray. The method does permit a beam of a certain kind of ions being sorted from the main beam of positive rays so that it would seem possible to throw a beam of $\overset{+++}{N}$, for instance, against tungsten. It might also be possible to focus a beam of $\overset{+}{N}_2$ on another beam of $\overset{-}{O}$; or a beam of $\overset{+++}{N}$ on a beam of $\overset{-}{O}_6$ and observe what takes place.

The Dissociation of Molecules of Moving Ions and the Dynamics of Chemical Reactions in Gases

According to Kirkby,[1] an electron is not only able to break up molecules into charged ions by collision, but it can break up a molecule like oxygen into its component atoms. The ionization of a molecule like oxygen requires much more energy than the breaking up of a molecule into neutral parts, and may be presumed to occur only when the velocity of the electron is sufficiently great. Positive ions may also have the power of dissociating molecules, and of bringing a gas into the active state, so that it can form new combinations. The experimental results of Kirkby lead to the conclusion that atoms of oxygen, when separated, are not charged electrically, so that there must be other than electrical forces that bind the atoms in the molecule together.

Kirkby has found that when a steady discharge passes through an electrolytic gas at a pressure p mm., the number of molecules of water vapor formed by the passage of an atomic charge through 1 cm. of the positive column where the electric force is E_x is $7.9\, pe - 42.7\, p/E_x$. The chemical effects in the positive column are due to the collisions of the electrons dissociating the oxygen molecules into atoms and under these conditions the oxygen atoms, when they collide with hydrogen molecules, unite with them to form water molecules.

In Kirkby's experiments, only about half of the collisions between electrons and oxygen molecules resulted in the formation of oxygen atoms. The energy of the formation of an oxygen molecule is given as 5.3×10^{-12} ergs, and of a molecule of water vapor as 6.4×10^{-12} ergs.

The collision constants[2] seem to be independent of the ionizing agent, as would be expected. The general theory of ionization by collision has also been found to apply to vapors as well as to gases if the pressure is not too high.

[1] P. Roy. Soc., A, **85**, 171 (1911).

[2] Barus: Am. J. Sci., **34**, 229 (1912).

At high temperatures the power consumption necessary to maintain a tungsten wire at a given temperature increases with abnormal rapidity with the temperature. Langmuir[1] considers that this energy is absorbed by the dissociating hydrogen gas near the wire, the hydrogen atoms again recombining after they diffuse some distance from the wire. The effect begins at 2100° C. (abs.) and the heat of the reaction is given at 130,000 calories.

Langmuir[2] considers that the oxidation of tungsten in an incandescent lamp bulb is not due to a direct reaction between the oxygen molecules and the tungsten atoms, but that the oxygen atoms must first become negatively charged by collision with electrons. Only electrons with a velocity exceeding 6×10^{-7} cm. per second are considered as being able to charge oxygen atoms. In a reaction of this type the velocity of the oxygen atoms is affected but little with rise in temperature of the tungsten filament so that the number of variables entering into the reaction can be considerably reduced.

It seems, therefore, that once the oxygen molecule is charged negatively, it can be held by the positively charged tungsten atoms and "secondary reactions" then take place, resulting in the formation of the oxide WO_3. The ratio between the number of oxygen molecules colliding with the tungsten filament and those combining with the tungsten to form the oxide WO_3 for the various temperatures of the filament is as follows:

Temperature (absolute)	Ratio observed	Ratio calculated
1070	0.00033	0.00016
1270	0.0011	0.0012
1470	0.0053	0.0052
1770	0.0255	0.0256
2020	0.049	0.066
2290	0.095	0.145
2520	0.12	0.26
2770	0.15	0.42

The calculated value based on the assumption that electrons are emitted by the tungsten with a Maxwell distribution of velocity and that the oxygen molecule unites with an electron exceeds that given above. W. W. STRONG

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[1] J. Am. Chem. Soc., **34**, 260 (1912).

[2] *Ibid.*, **35**, 126 (1913).

REVIEWS

Traité de Chimie Minérale. Par H. Erdman, Directeur de l'Institut de Chimie Minérale de la Technische Hochschule de Berlin. Ouvrage traduit sur la 5e Édition allemande par A. Corvisy, Professeur Aggrégé des Sciences Physiques au Lycée Gay-Lussac, Professuer Suppléant à l'Ecole de Médecine et de Pharmacie de Limoges. Tome Premier. Introduction à la Chimie et Métalloides. Avec 243 figures et 2 planches spectrales coloriées. Paris: Librairie Scientifique A. Hermann et Fils. 1913. pp. iv + 559. Price, Fr. 12.00.

French chemists are to be congratulated upon now having at their disposal this translation of Erdmann's well-known book. The ability of Prof. Corvisy as a translator has already been shown in the French versions prepared by him of Ladenburg's "History" and "Nernst's Theoretical Chemistry." The type and illustrations in the present volume are clear, the paper good. C. A. R.

Les Nouveautés Chimiques pour 1913. Nouveaux Appareils de Laboratoires, Méthodes Nouvelles de Recherches Appliquées à la Science et à l'Industrie. Par Camille Poulenc, Docteur es Sciences. Avec 195 Figures intercalées dans le Texte. Paris: J. B. Baillière et Fils. 1913. pp. viii + 329. Price, Fr. 4.00.

The present volume, the eighteenth of this useful annual, is, as usual, divided into five chapters under the following headings and subheadings: I. General Applications of Physics to Chemistry (63 pp.): Determination of Densities; Determination of Temperatures; Determination of Melting Points; Calorimetry; Microscopy; Colorimetry; Spectroscopy. II. Miscellaneous Laboratory Apparatus (65 pp.): Heating Apparatus; Distillation Apparatus; Extraction Apparatus; Apparatus for the Production of Gases; Apparatus for Producing a Vacuum or Compressed Air; Filtration Apparatus; Miscellaneous Apparatus. III. Electricity (16 pp.): Heating Apparatus; Miscellaneous Apparatus. IV. Chemical Analysis (141 pp.); General Analytical Apparatus, Burettes, Pipettes, etc.; Miscellaneous Apparatus; Industrial Analyses, Gas Analyses, Miscellaneous Analyses, Apparatus for the Detection or Separation of Arsenic, Metallurgy, Analyses of Alimentary Substances, Medical Analyses. V. Bacteriology (25 pp.); Apparatus for Sterilization or Cultures; Apparatus for Keeping or for Taking Samples for Bacteriological Investigation; Miscellaneous Apparatus.

The book is well worth looking through. C. A. R.

Chemical Theory and Calculations. An Elementary Text-Book. By Forsyth James Wilson, D.Sc. (Edin.), Ph.D. (Leipzig), and Isidor M. Heilbron, Ph.D. (Leipzig), F.I.C., A.R.T.C., Lecturer in

Chemistry, the Royal Technical College, Glasgow. New York: D. Van Nostrand Co. 1912. pp. 138. Price, $1.00.

This little book is divided into twenty-one chapters, which cover pretty thoroughly all phases of elementary chemistry involving arithmetical operations, beginning with "The Metric System" and ending with "Thermochemistry" and including such subjects as "Valency" and "The Periodic Classification of the Elements," which are not usually included in "chemical arithmetics." In each chapter the theory of the subject dealt with is briefly developed and numerous problems of a practical nature are given. The treatment throughout seems to be quite clear.

C. A. R.

WHO'S WHO IN SCIENCE, INTERNATIONAL, 1913. Edited by H. H. STEPHENSON. London: J. and A. Churchhill. pp. xvi + 569. Price, $3.50.

New features in this issue of the international "Who's Who in Science," are a section on "The World's Societies" (including name, address, president and secretary, date of foundation, number of members, annual subscription and periodical publications) and a frontispiece consisting of portraits of prominent scientists who have died in the preceding year (van't Hoff, Hooker, Lister, Poincaré, Strassburger). Psychology and Geography have been added to the sciences represented. Besides these, the book contains an "Obituary for 1912;" a section on "The World's Universities," giving the site, date of foundation, president, registrar and senior professors of the different departments; "Biographies;" and a "Classified Index" in which the names of the men whose biographies are given are grouped under subjects and these groups again subdivided into nationalities. Great Britain is naturally better represented than other countries; thus, under "Chemistry, Pure and Applied," we find the names of 126 German, 281 British, 228 American and only 42 French and 12 Italian chemists.

C. A. R.

FORTSCHRITTE UND PROBLEME DER CHEMISCHEN INDUSTRIE. Vortrag, gehalten in der allgemeinen Sitzung des VIII Internationalen Kongresses für Angewandte Chemie am 9 September, 1912, in New York. Von C. DUISBERG. Leipzig: Verlag von Otto Spamer. 1913. p. 32.

A debt of thanks is due to the publishers for making available, in such convenient form, this interesting and authoritative, though necessarily brief, review of the most recent advances made and the more important problems now being studied in the field of industrial chemistry.

C. A. R.

EVANS' ANALYTICAL NOTES FOR 1912. From the Laboratories of EVANS' SONS, LESCHER AND WEBB, Limited, Wholesale and Export Druggists and Manufacturing Chemists, Liverpool and London. No. 7. 92 William St., New York. March, 1913. pp. 100.

The following words are taken from the preface: "...... the researches of science are being employed in an illegitimate as well as in a legitimate direction to help the manufacturer. ...... During the years under review (1912) upwards of 10,000 samples have passed through the hands of our Analytical Laboratory, and the notes now presented form a *precis* of the more interesting examinations made and the researches undertaken by our chief chemist, Mr. H. R. Jensen, B.Sc., and his assistants. The necessity for analytical control in all directions is made obvious by the fact that of the 2,400 samples herein referred to, 250 were reported upon as falling below the standard. It must also be borne in mind that such control tends to raise the standard of samples submitted to us.

"Tables dealing with melting points, volumetric equivalents, resin constants and impurity limits have been carefully compiled, and together with the oil tables, which have been revised up to date, form an appendix to the notes." C. A. R.

REPORT OF LEHN AND FINK'S ANALYTICAL DEPARTMENT FOR 1910-1912. By HORACE NORTH, assisted by F. H. SCHORTEMEYER. New York: Lehn & Fink, Wholesale Druggists and Manufacturing Chemists. January, 1913. pp. 98.

Lehn and Fisk take a more optimistic view of the state of the drug industry than the English firm whose analytical report is noticed above. They say: "Some of the more interesting work of the past three years is reviewed in the following pages.. While the notes are somewhat discursive, it is believed that they will, in many cases, prove suggestive. Data on a long series of samples received at various times from various sources necessarily afford a broader survey of the status of any given drug than the occasional analyses of chemists bent on pure research. For the most part, the outlook is encouraging; the drug market was never in a more satisfactory state than at the present time. The majority of drugs comply with the law. Certain drugs are peculiarly subject to adulteration; for example, asafetida and lupulin, and much patient effort must still be expended before such drugs can be brought up to the required standard." C. A. R.